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STRUCTURE AND MOLECULAR FORCES IN (a) *PURE LIQUIDS AND* (b) *SOLUTIONS*

GENERAL DISCUSSION

HELD BY

The Faraday Society

September, 1936

(*For Table of Contents and Author Index see page 280*)

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CONTENTS OF PART 1

Einflüsse der Strömung, Diffusion und des Wärmeüberganges auf die Leistung von Reaktionsöfen. II. Die isotherme, raumbeständige, homogene Reaktion erster Ordnung. Von *G. Damköhler.*

Einflüsse der Strömung, Diffusion und des Wärmeüberganges auf die Leistung von Reaktionsöfen. III. Zur Frage der maximalen Uebertemperatur in einem rohrförmigen Kontaktofen bei exothermen Reaktionen. Von *G. Damköhler.*

Die Flüchtigkeit der Borsäure mit Wasserdampf. Das System B_2O_3-Wasser. Von *M. v. Stackelberg, F. Quatram* und *Julia Dressel.*

Zur Theorie binärer Lösungen. Eine Ergänzung zu der gleichnamigen Arbeit von E. Hückel. Von *Karl Fredenhagen.*

Zur Passivität des Chroms. V. Von *Erich Müller* und *V. Čupr.*

Ueber Struktur und Wärmeinhalt verschieden dargestellter γ-Eisen (III.) oxyde, sowie über die Bildungswärme des Lepidokrokit (γ—FeOOH). 12. Mitteilung über Struktur, Wärmeinhalt und sonstige Eigenschaften aktiver Stoffe. Von *R. Fricke* und *W. Zerrweck.*

Ueber die thermische Dissoziation des Blei (4)-oxyds. Von *J. Krustinsons.*

Eine einfache Methode zur Herstellung von Leitfähigkeitswasser höchsten Reinheitsgrades. Von *P. A. Thiessen* und *K. Herrmann.*

A GENERAL DISCUSSION ON STRUCTURE AND MOLECULAR FORCES IN (*a*) PURE LIQUIDS AND (*b*) SOLUTIONS.

Thursday, 24th, to Saturday, 26th September, 1936.

The Sixty-Fifth General Discussion of the Faraday Society was held in the Department of Chemistry of the University of Edinburgh from Thursday to Saturday, 24th to 26th September, 1936, inclusive.

The subject was considered under the following heads:

(*a*) Structure and Molecular Forces in Pure Liquids.
(*b*) Structure and Molecular Forces in Solutions.

Before the commencement of the proceedings Professor F. G. Donnan, Past President, referred to the Society's recent loss by the death of the President, Mr. William Rintoul, and those present stood for a few moments in homage to his memory.

Professor James Kendall, having welcomed the Society to Edinburgh on behalf of the University authorities, Mr. H. A. Ruffel, the President of the University of Edinburgh Chemical Society, conferred the Honorary Membership of the Society on Professor Donnan and on Professor J. H. Hildebrand of the University of California. The Chair was then taken by Professor Donnan, and in the later sessions by Professor Kendall.

At the inaugural meeting Professor Donnan welcomed the overseas guests and members, who were received with acclamation; those so welcomed were: Dr. E. Bartholomé (*Gottingen*), Professor E. Bauer (*Paris*), Dr. P. Bignard (*Paris*), Professor L. Brillouin (*Paris*), Dr. H. C. Brinkman (*Amsterdam*), Dr. J. M. Burgers and Mrs. Burgers (*Delft*), Dr. [illegible] (*Liège*), Professor J. Errera (*Brussels*), Professor L. Farkas (*Jerusalem*), Dr. P. Gross (*Wien*), Professor V. Henri (*Liège*), Professor J. H. Hildebrand and Mrs. Hildebrand (*Berkeley, California*), Dr. A. Klinkenberg (*The Hague*), Frl. Dr. D. Kruger (*Berlin*), Dr. H. Limburg (*Amsterdam*), Professor F. London (*Paris*), Dr. R. Lucas (*Paris*), Dr. M. Magat (*Paris*), Monsieur M. Mathieu (*Paris*), Professor J. A. Prins (*Wageningen*), Professor R. A. Robinson (*Auckland, N.Z.*), Dr. H. Sack (*Brussels*), Dr. G. Salomon (*Zürich*) and Dr. W. R. van Wijk (*Amsterdam*).

By the courtesy of the Vice-Chancellor and of the Principal Warden the members and guests visiting Edinburgh were accommodated in the Carlyle Hostel for Women Students, where the Guest Night Dinner was held on Friday, 25th September.

The Report of the meeting, including all the papers contributed, together with the discussion thereon, appears in the following pages.

PURE LIQUIDS AND LIQUID MIXTURES.
(General Introductory Paper.)

By James Kendall.

Received 3rd September, 1930.

This General Discussion on the structure and molecular forces in pure liquids and solutions provides the Faraday Society with an excellent opportunity to enlighten chemists upon the tremendous changes which have taken place in recent years with regard to our fundamental conceptions in this field. It is astonishing, when we consider how far speculations have been carried into the nature of complex solutions, particularly of strong electrolytes, how little attention is still paid by the majority of investigators to the case of the simple solvent. It is even more astonishing to find, by a perusal of current articles, how many research workers who are familiar with all the refinements which the Debye-Hückel theory has imposed upon the classical ideas of Arrhenius are still totally unaware of the fact that the Van't Hoff analogy between dilute solutions and gases has long ago been discarded.

The width of the discussion has proved a source of considerable difficulty, and in order to avoid congestion of the programme it has been necessary to omit certain of the papers submitted. The general principle followed has been not to include communications dealing with subjects, such as Dipole Moments and the Theory of Strong Electrolytes, which have formed the basis of recent meetings. Kinetics, which will constitute the topic of a forthcoming symposium, has also been excluded. In several border-line cases, however, mercy may have marred consistency, and it is hoped that those whose articles do not appear on the final programme will also be merciful in their comment upon the sub-committee's action.

The hard-and-fast distinction between the solid, liquid and gaseous states—to which the liquid-vapour critical point formerly supplied the only exception—has now largely disappeared. The transition from the liquid to the solid state proves to be by no means so sudden as the "simple" phenomenon of freezing has led us to postulate, and adsorption experiments have indicated definite intermediate steps even between crystals and gases. In spite of this merging of the three states of matter towards one theoretical continuity, nevertheless, it is certain that for many practical considerations the perpetuation of the distinction between them will remain. That the forces between "liquid" and "gaseous" molecules influence their behaviour in quite diverse ways may be seen by examining briefly one particular physical property—viscosity. The viscosity of a liquid decreases as the temperature is raised; the viscosity of a gas increases. The viscosity of a liquid increases with pressure (except, luckily for city water supplies, in the case of water at low temperatures, where it decreases); the viscosity of a gas is unaffected by pressure. The viscosity curve of ideal liquid mixtures sags far below the straight line joining the viscosities of the two components; the viscosity curve of ideal gaseous mixtures shows a hump like a dromedary. In every respect the two states of matter show fundamental differences, and although the theory of gaseous viscosity was worked out in 1860 by Clerk Maxwell, we are only now beginning to understand the more complicated case of liquids.

The close packing of molecules in the liquid state renders intermolecular forces much greater than those between gaseous molecules. In the past, however, it has been customary to consider such forces as essentially similar in their nature, *i.e.*, either ordinary Van der Waals' attractions (where no particular complex groupings ensued) or valence forces (where electron exchange led to the formation of definite associated molecules). The introduction of the conception of dipoles (permanent and induced) has destroyed this simple formulation for ordinary liquids, while for electrolytes the coulomb forces, and for metals the metallic cohesive forces, must also now be taken into account. The conception of definite associated groups is much less popular now than formerly. At a General Discussion held by this Society on the Constitution of Water in 1910 my distinguished predecessor, Sir James Walker, summed up the unanimous decision of the meeting as follows:[1] "Whilst ice is trihydrol, and steam monohydrol, liquid water is mostly dihydrol with some trihydrol in it near the freezing-point, and a little monohydrol near the boiling-point." Nowadays the majority of physical chemists, probably, would subscribe rather to the idea of Langmuir that the whole ocean consists of one loose molecule, and that the removal of a fish therefrom is a dissociation process. Even in the case of liquid mixtures, from which definite complexes can be isolated by freezing, it seems that the associated groups present in the liquid state are not necessarily identical with those which appear in the crystalline state.

It is now more than forty years since Van Laar promulgated the theory of ideal solutions, subsequently more simply restated by G. N. Lewis and Washburn, but the standard text-books still rear most students in the ingenious, but erroneous, creed of Van't Hoff. If the solute in a dilute liquid solution were, indeed, in the gaseous state, then a gas (disregarding the volume change) should have zero heat of solution, while for a liquid and a solid the heat of solution should approximate to the heat of vaporisation and to the heat of sublimation respectively. Experiment shows that this is not so. In the ideal case, where no special factors arise, the heat of solution of a gas is equal to its heat of condensation, the heat of solution of a liquid is zero, and the heat of solution of a solid is equal to its heat of fusion. In other words, any substance dissolved in a liquid itself assumes the liquid state. For a solid like sugar, melting and dissolving are synonymous terms, and it is just as correct to say that sugar melts in tea as it is to say that ice melts in an iced drink.

Unfortunately, ideal solutions are almost as rare in practice as infinitely dilute solutions, and in most liquid mixtures the deviations from the simple law of Raoult are considerable. The cause of such deviations has been most intensively studied by Hildebrand in connection with the magnitude of the forces between the molecules in the solution. Where solvent and solute molecules have a smaller attraction than solvent molecules alone, a "squeezing-out tendency" of the solute is noticeable, leading in extreme cases to the formation of two liquid layers and, even when complete miscibility persists, involving positive deviations (abnormally small vapour pressure lowering and freezing-point depression) from Raoult's law. Under the classical theory, such positive deviations were invariably attributed to association of the solute into complex molecules, but probably 99 per cent. of all published work on association in the liquid state is illusory. The prize instance, perhaps, is the conclusion by Dolezalek[2] that argon is polymerised to A_2 when dissolved in liquid nitrogen. The quantitative and logical explanation of these positive deviations by Hildebrand, on the basis of internal pressure differences, is worthy of greater recognition than it has yet received.

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[1] *Trans. Faraday Soc.*, 1910, 6, 143.

Negative deviations from Raoult's law signify very great attractive forces between solvent and solute molecules, and it is noteworthy that abnormally large freezing-point depressions are always provided by such systems where these attractive forces are sufficient to induce the formation of definite compounds. Even if we concede the fact, alluded to previously, that the compounds isolated by freezing are not necessarily identical with those existent in the solution, the parallelism between the extent of compound formation and the magnitude of the negative deviations in a long series of systems is far too striking to be due entirely to chance.[3] The compounds formed fall into two types: (*a*) addition compounds, (*b*) substitution compounds, and general rules have been deduced relating the stability of each type with the nature of the components of the solution. For details, reference should be made to the original communications.[4]

In a few systems, anomalous as it may seem, both positive and negative deviations occur, counterbalancing each other to furnish "pseudo-ideal" freezing-point depression curves. Two examples of this type are provided by the systems ethyl ether-water and ethyl acetate-water. The internal pressures of the organic substances are so low, relative to that of water, as to induce partial miscibility. On the other hand, the evolution of heat and the contraction of volume on admixture (a saturated solution of ethyl acetate in water at 0° has a density greater than unity) are strong indications of chemical interaction. This interaction probably consists, in the case of ether, in a substitution of part of the H_2O in $(H_2O)_x$ by the similar group $(C_2H_5)_2O$. In the case of ethyl acetate, the formulation is not so obvious, but it appears that only the nature of the acidic group has any significant effect on the extent of compound formation.[5] The remainder of this paper presents the results of a study of these two systems carried out under the author's direction by Dr. Attisani and Dr. Olsen, of Washington Square College, New York University. Since the experimental data are essentially similar, the curves for the system ethyl acetate-water only will be discussed in detail.

The freezing-point depression and solubility curves of ethyl acetate in pure water are shown at the top of Fig. 1. It will be seen that they intersect at about − 2°, where the molecular per cent. of ester is about 2, and it is impossible to carry the freezing-point depression curve in pure water beyond that concentration. It was thought, however, that addition of ethyl alcohol to the system might remove this barrier. The

[2] *Z. physik. Chem.*, 1918, **93**, 585.

[3] See, for example, Kendall, Davidson and Adler, *J. Amer. Chem. Soc.*, 1921, **43**, 1481.

[4] *E.g.*, Kendall, *Proc. Nat. Acad. Sci.*, 1921, **7**, 56; Kendall and Beaver, *J. Amer. Chem. Soc.*, 1921, **43**, 1853.

[5] Kendall and Harrison, *Trans. Faraday Soc.*, 1928, **24**, 588.

presence of alcohol would be expected (*a*) to move the solubility curve towards the right, and (*b*) to push the freezing-point curve downwards, bringing their point of intersection to a much higher concentration of ester. In fact, it was hoped that a few molecular per cent. of alcohol would suffice to prevent the two curves from intersecting at all, thus enabling a complete examination of the ester-water system to be made and ensuring the isolation of the anticipated compound.

The actual results were quite different, as will be seen by examination of Figs. 1-3. Each curve in these diagrams represents the freezing-points of a series of mixtures containing a constant molecular per cent. of ethyl alcohol, ice being the solid phase throughout. The composition scale is necessarily changed in each diagram, but the "carry-over" of curves from one figure to another facilitates any comparisons which may be desired.

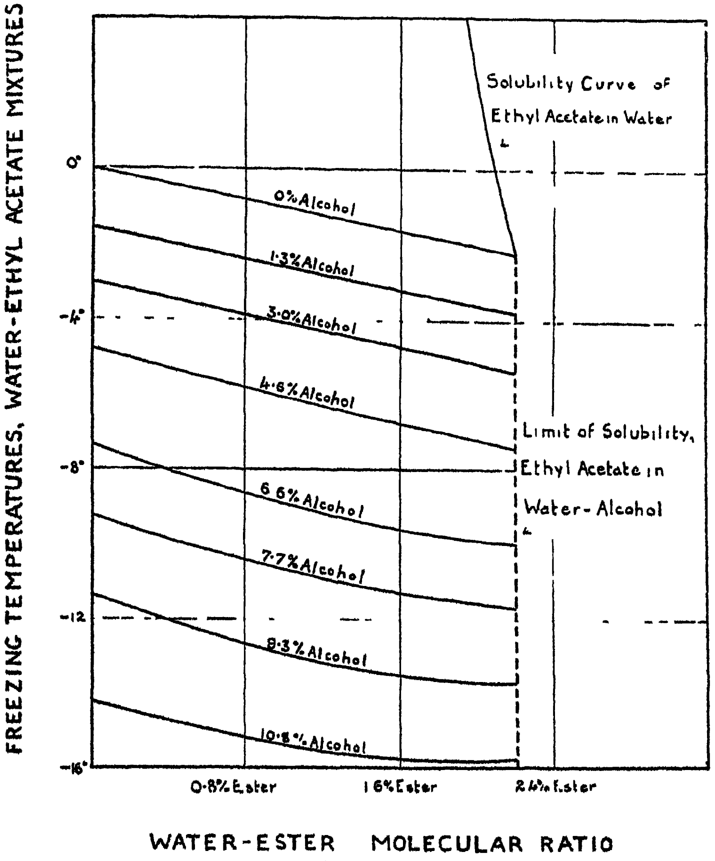

FIG. 1.

It will be seen from Fig. 1 that the addition of alcohol, up to 10·8 molecular per cent., does *not* increase the solubility of ethyl acetate in water. Indeed, when we note that lowering the temperature should itself involve a considerable increase in solubility, we may regard the presence of the alcohol as *diminishing* the miscibility. The isotherm for the three-component system at 0°, in fact, shows that the first addition of ethyl alcohol does lower the solubility of ethyl acetate in water.[6] This "salting-out effect" of alcohol on mixtures of ethyl acetate (or ether) and water will be no less surprising to organic than to physical chemists. Soon after the alcohol concentration, however, exceeds 10·8 molecular per cent., ester-water miscibility increases rapidly, and Fig 2 shows that mixtures containing more than 20 molecular per cent. of alcohol (approximately) are miscible in all proportions.

In the meantime, the freezing-point depression curve has been behaving in a most peculiar manner. We should expect increasing miscibility and increasing compound stability to make this curve steeper at lower temperatures. Instead, it flattens out, first gradually, then more rapidly, until at 10·8 per cent. of alcohol it shows a minimum.

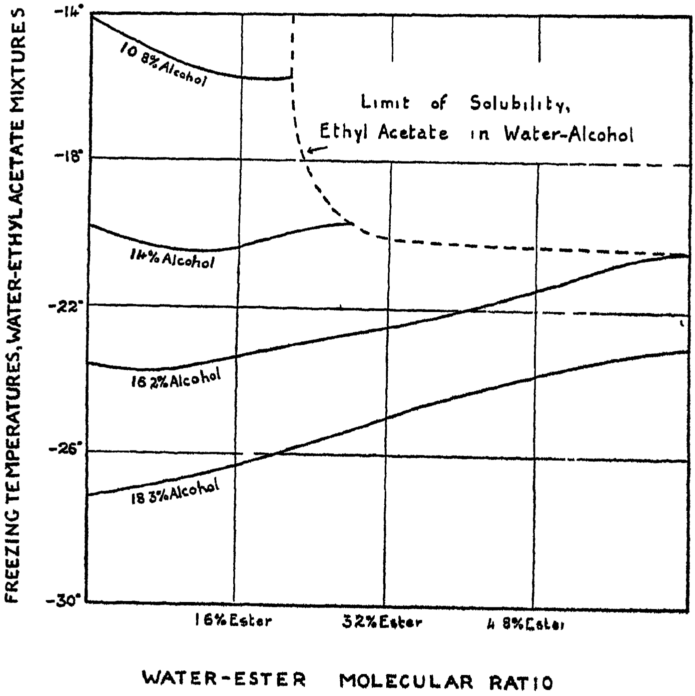

FIG. 2.

Beyond 10·8 per cent. of alcohol the minimum deepens and moves to lower concentrations of ester, and after 18·3 per cent. of alcohol has been added the curve ascends towards higher temperatures from the very start. Examination of Fig. 3 discloses the startling fact that addition of 30 molecular per cent. of ethyl acetate to water, when each is "doped" with 26·5 molecular per cent. of alcohol, raises the temperature at which ice begins to separate out from the solution by nearly 10°! In the ethyl ether-water system, similarly, addition of 45 molecular per cent. of ether to water, each containing 24 molecular per cent. of alcohol, raises the freezing-point more than 12°. In neither case was it found possible to isolate any compounds from the solution.

[6] See *International Critical Tables*, 1928, 3, 412.

The full significance of these bewildering results cannot be deduced at present; vapour pressure data for the complete ternary systems at two or three fixed temperatures are needed to support any tentative explanation that might be advanced. The value of the investigation as it stands consists in the striking proof that it affords that environmental changes affect the physical properties of liquid mixtures to an enormous extent. As a further illustration of this point, the fact that the addition of 1 molecular per cent. of ethyl acetate to an aqueous solution of an acid or a neutral salt reduces its specific conductivity by about 20 per cent.[7] may be cited. Until proper attention is paid to phenomena such as these, no advances can possibly be made in our knowledge of that much laboured field, the mechanism of ester hydrolysis. Many other equally important questions in physical chemistry must remain unanswered until we learn much more than we now know about the nature and the magnitude of molecular forces existent in solutions. It is hoped that the present symposium will serve to stimulate progress in this direction.

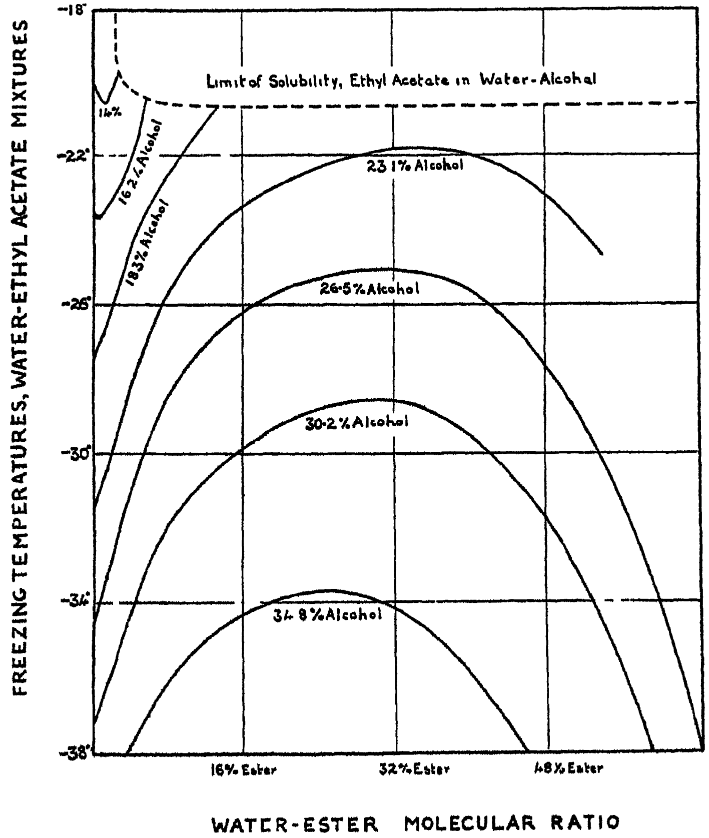

FIG. 3.

Department of Chemistry,
University of Edinburgh.

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[7] Kendall and King, *J. Chem. Soc.*, 1925, 127, 1778.

GENERAL DISCUSSION.

Dr. S. Glasstone (*Sheffield*) said : The surprising results reported by Professor Kendall on the effect of ethyl alcohol on the solubility of ethyl acetate in water may perhaps be explained as follows. Since the internal pressures of ethyl acetate and water are so different, the solubility of the former would be very small were it not for compound formation which occurs between the two components : this compound formation probably involves a hydrogen bond between the water molecule and one of the oxygen atoms of the ester. The water may be regarded as consisting effectively of a large associated molecule, in accordance with the views of Bernal and Fowler,[8] and of Sidgwick,[9] and only a small proportion of simple water molecules will be " free " to participate in compound formation. The addition of alcohol at first provides a competitor for these water molecules, since alcohol–water complexes undoubtedly exist, so that smaller amounts of ethyl acetate can form the compound essential for the dissolution in water ; the quantity dissolved consequently decreases. When relatively large proportions of alcohol are present, however, the normal solubility influence of the latter on ethyl acetate, partly due to its internal pressure and partly to the tendency to form alternative compounds, asserts itself and the solubility of the ester increases. Vapour pressure measurements of the ethyl alcohol–water–ethyl acetate system might provide confirmation for this explanation of the observations. In any case, it would be of interest to know whether the solid phase which separated on freezing the solutions was always ice, or whether any compounds were obtained.

Professor K. L. Wolf (*Würzburg*) (*communicated*) : I would refer to Fredenhagen's investigations which provide many examples where the original theory of osmotic pressure does not apply.[10]

Professor J. Kendall (*Edinburgh*) said : In reply to Dr. Glasstone's question whether the solid phase was ice throughout : Yes ; there were no indications either of compounds or of solid solutions.

[8] *J. Chem. Physics*, 1933, **1**, 515.
[9] *Ann. Reports Chem. Soc.*, 1934, **31**, 42.
[10] K. Fredenhagen, *Z. ges. Naturwiss.*, 1935, **1**, 278.

THE GENERAL THEORY OF MOLECULAR FORCES.

By F. London (*Paris*).

Received 31*st* *July*, 1936.

Following Van der Waals, we have learnt to think of the molecules as centres of forces and to consider these so-called *Molecular Forces* as the common cause for various phenomena : The deviations of the gas equation from that of an ideal gas, which, as one knows, indicate the identity of the molecular forces in the liquid with those in the gaseous state ; the phenomena of capillarity and of adsorption ; the sublimation heat of molecular lattices ; certain effects of broadening of spectral lines, etc. It has already been possible roughly to determine these forces in a fairly consistent quantitative way, using their measurable effects as basis.

In these semi-empirical calculations, for reasons of simplicity, one imagined the molecular forces simply as rigid, additive central forces, in general cohesion, like gravitation ; this presumption actually implied a very suggestive and simple explanation of the parallelism observed in the different effects of these forces. When, however, one began to try to explain the molecular forces by the general conceptions of the electric structure of the molecules it seemed hopeless to obtain such a simple result.

§ 1. Orientation Effect.[1]

Since molecules as a whole are usually uncharged the *dipole moment* μ was regarded as the most important constant for the forces between molecules. The interaction between two such dipoles μ_{I} and μ_{II} depends upon their relative orientation. The interaction energy is well known to be given to a first approximation by

$$U = -\frac{\mu_{\mathrm{I}}\mu_{\mathrm{II}}}{R^3}(2\cos\theta_{\mathrm{I}}\cos\theta_{\mathrm{II}} - \sin\theta_{\mathrm{I}}\sin\theta_{\mathrm{II}}\cos(\phi_{\mathrm{I}} - \phi_{\mathrm{II}})) \qquad (1)$$

where $\theta_{\mathrm{I}}, \phi_{\mathrm{I}}$; $\theta_{\mathrm{II}}, \phi_{\mathrm{II}}$ are polar co-ordinates giving the orientation of the dipoles, the polar axis being represented by the line joining the two centres, $R =$ their distance. We obtain attraction as well as repulsion, corresponding to the different orientations. If all orientations were equally often realised the average of μ would be zero.

But according to Boltzmann statistics the orientations of lower energy are statistically preferred, the more preferred the lower the temperature. Keesom, averaging over all positions, found as a result of this preference:

$$\bar{U} = -\frac{2}{3}\frac{\mu_{\mathrm{I}}^2\mu_{\mathrm{II}}^2}{R^6}\frac{1}{kT} \qquad \left(\text{valid for } \frac{\mu_{\mathrm{I}}\mu_{\mathrm{II}}}{R^3} \ll kT\right). \quad . \quad (2)$$

For low temperatures or small distances $\left(kT \lesssim \frac{\mu_{\mathrm{I}}\mu_{\mathrm{II}}}{R^3}\right)$ this expression does not hold. It is obvious that the molecules cannot have a more favourable orientation than parallel to each other along the line joining the two molecules, in which case one would obtain as interaction energy (see (1)):

$$\bar{U} = -\frac{2\mu_{\mathrm{I}}\mu_{\mathrm{II}}}{R^3} \qquad \left(\text{valid for } \frac{\mu_{\mathrm{I}}\mu_{\mathrm{II}}}{R^3} \gg kT\right) \quad . \quad . \quad (3)$$

which gives in any case a lower limit for this energy. (2) and (3) represent an attractive force, the so-called *orientation effect*, by which Keesom tried to interpret the Van der Waals attraction.

§ 2. Induction Effect.[2]

Debye remarked that these forces cannot be the only ones. According to (2) they give an attraction which vanishes with increasing temperature. But experience shows that the empirical Van der Waals corrections do not vanish equally rapidly with high temperatures, and Debye therefore concluded that there must be, in addition, an interaction energy independent of temperature. In this respect it would not help to consider the actual charge distribution of the molecules more in detail,

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[1] W. H. Keesom, *Leiden Comm. Suppl.*, 1912, **24a**, **24b**, **25**, **26**; 1915, **39a**, **39b**. *Proc. Amst.*, 1913, **15**, 240, 256, 417, 643; 1916, **18**, 636; 1922, **24**, 162. *Physik. Z.*, 1921, **22**, 129, 643; 1922, **23**, 225.

[2] P. Debye, *Physik. Z.*, 1920, **21**, 178; 1921, **22**, 302. H. Falckenhagen, *Physik. Z.*, 1922, **23**, 87.

e g. by introducing the quadrupole and higher moments. The average of these interactions also would vanish for high temperatures.

But by its charge distribution alone a molecule is, of course, still very roughly characterised. Actually, the charge distribution will be changed under the influence of another molecule. This property of a molecule can very simply be described by introducing a further constant, the *polarisability* α. In an external electric field of the strength F a molecule of polarisability α shows an *induced* moment

$$M = \alpha \, . \, F \quad . \quad . \quad . \quad . \quad . \quad (4)$$

(in addition to a possible *permanent* dipole moment) and its energy in the field F is given by

$$U = - \tfrac{1}{2}\alpha \, . \, F^2 \quad . \quad . \quad . \quad . \quad (5)$$

Now the molecule I may produce near the molecule II an electric field of the strength

$$F = \frac{\mu_I}{R^3} \sqrt{1 + 3 \cos^2 \theta_I} \quad . \quad . \quad . \quad . \quad (6)$$

This field polarises the molecule II and gives rise to an additional interaction energy according to (5)

$$U = - \tfrac{1}{2}\alpha_{II} F^2 = - \frac{\alpha_{II}}{2} \frac{\mu_I^2}{R^6}(1 + 3 \cos^2 \theta_I) \quad . \quad . \quad (7)$$

which is always negative (*attraction*) and therefore its average, even for infinitely high temperatures, is also negative. Since $\cos^2 \theta = \frac{1}{3}$ we obtain:

$$\bar{U}_{I \rightarrow II} = - \alpha_{II} \frac{\mu_I^2}{R^6}$$

A corresponding amount would result for $\bar{U}_{II \rightarrow I}$, *i.e.* for the action of μ_{II} upon α_I. As total interaction of the two molecules we obtain:

$$\bar{U} = - \frac{1}{R^6}(\alpha_I \mu_{II}^2 + \alpha_{II} \mu_I^2) \quad . \quad . \quad . \quad (8)$$

If the two molecules are of the same kind ($\mu_I = \mu_{II} = \mu$ and $\alpha_I = \alpha_{II} = \alpha$) we have

$$\bar{U} = - \frac{2\alpha\mu^2}{R^6}. \quad . \quad . \quad . \quad . \quad . \quad (8')$$

This is the so-called *induction effect.*

In such a way Debye and Falckenhagen believed it possible to explain the Van der Waals equation. But many molecules have certainly no permanent dipole moment (rare gases, H_2, N_2, CH_4, etc.). There they assumed the existence of quadrupole moments τ, which would of course also give rise to a similar interaction by inducing dipoles in each other. Instead of (8) this would give:

$$\bar{U} = - \frac{3}{2} \frac{\alpha\tau^2}{R^8}. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Since no other method of measuring these quadrupoles was known, the Van der Waals corrections (second Virial coefficient) were used in order to determine backwards τ, which, after μ and α, has been regarded as the most fundamental molecular constant.

§ 3. Criticism of the Static Models for Molecular Forces.

The most obvious objection to all these conceptions is that they do not explain the above mentioned parallelism in the different manifestations of the molecular forces. One cannot understand why, for example, in the liquid and in the solid state between all neighbours simultaneously practically the same forces should act as between the occasional pairs of molecules in the gaseous state. All these models are very far from simply representing a general additive cohesion:

Suppose that two molecules I and II have such orientations of their permanent dipoles that they are attracted by a third one; then between the two former molecules very different forces are usually operative, mostly repulsive forces. Or, if the forces are due to polarisation, the acting field will usually be greatly lowered, when many molecules from different sides superimpose their polarising fields. One should expect, therefore, that in the liquid and in the solid state the forces caused by induced or permanent dipoles or multipoles should at least be greatly diminished, if not by reasons of symmetry completely cancelled.

The situation seemed to be still worse when wave mechanics showed that the rare gases are exactly spherically symmetrical, that they have neither a permanent dipole nor quadrupole nor any other multipole. They showed none of the mentioned interactions. It is true, that for H_2, N_2, etc., wave mechanics, too, gives at least quadrupoles. But for H_2 we are now able to calculate the value of the quadrupole moment numerically by wave mechanics. One gets only about 1/100 of the Van der Waals forces that were attributed hitherto to suitably chosen quadrupoles.

On the other hand, wave mechanics has provided us with a completely new aspect of the interaction between neutral atomic systems.

§ 4. Dispersion Effect; a Simplified Model.[3]

Let us take two spherically symmetrical systems, each with a polarisability α, say two three-dimensional isotropic harmonic oscillators with no permanent moment in their rest position. If the charges e of these oscillators are artificially displaced from their rest positions by the displacements

$$\vec{r}_{I} = (x_{I}, y_{I}, z_{I}) \quad \text{and} \quad \vec{r}_{II} = (x_{II}, y_{II}, z_{II})$$

respectively, we obtain for the potential energy:

$$V = \underbrace{\frac{e^2 r_I^2}{2\alpha} + \frac{e^2 r_{II}^2}{2\alpha}}_{\text{Elastic Energy.}} + \underbrace{\frac{e^2}{R^3}(x_I x_{II} + y_I y_{II} - 2 z_I z_{II})}_{\text{Dipole Interaction Energy } (cf.\ (1)).} \quad . \quad . \quad (10)$$

Classically the two systems in their equilibrium position

$$(x_{I} = x_{II} = \ .\ .\ .\ = z_{II} = 0)$$

would not act upon each other and, when brought into finite distance ($R > \sqrt[3]{2\alpha}$), remain in their rest position. They could not influence a momentum in each other.

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[3] F. London, *Z. physik. Chem.*, 1930. *B*, 11, 222.

However, in *quantum mechanics*, as is well known, a particle cannot lie absolutely at rest on a certain point. That would contradict the uncertainty relation. According to quantum mechanics our isotropic oscillators, even in their lowest states, make a so-called *zero-point motion* which one can only describe statistically, for example, by a probability function which defines the probability with which any configuration occurs; whilst one cannot describe the way in which the different configurations follow each other. For the isotropic oscillators these probability functions give a spherically symmetric distribution of configurations round the rest position. (The rare gases, too, have such a spherically symmetrical distribution for the electrons around the nucleus.)

We need not know much quantum mechanics in order to discuss our simple model. We only need to know that in quantum mechanics the lowest state of a harmonic oscillator of the proper frequency ν has the energy

$$E_0 = \tfrac{1}{2}h\nu \quad . \quad . \quad . \quad . \quad . \quad (11)$$

the so-called *zero-point energy*. If we introduce the following co-ordinates ("normal"-co-ordinates):

$$\vec{r}_+ \equiv \begin{cases} x_+ = \frac{1}{\sqrt{2}}(x_{\text{I}} + x_{\text{II}}) \\ y_+ = \frac{1}{\sqrt{2}}(y_{\text{I}} + y_{\text{II}}) \\ z_+ = \frac{1}{\sqrt{2}}(z_{\text{I}} + z_{\text{II}}) \end{cases} \qquad \vec{r}_- \equiv \begin{cases} x_- = \frac{1}{\sqrt{2}}(x_{\text{I}} - x_{\text{II}}) \\ y_- = \frac{1}{\sqrt{2}}(y_{\text{I}} - y_{\text{II}}) \\ z_- = \frac{1}{\sqrt{2}}(z_{\text{I}} - z_{\text{II}}) \end{cases}$$

the potential energy (10) can be written as a sum of squares like the potential energy of six independent oscillators (while the kinetic energy would not change its form):

$$\begin{aligned} V &= \frac{e^2}{2\alpha}(r_+^2 + r_-^2) + \frac{e^2}{2R^3}(x_+^2 + y_+^2 - 2z_+^2 - x_-^2 - y_-^2 + 2z_-^2) . \\ &= \frac{e^2}{2\alpha}\Big[\Big(1 + \frac{\alpha}{R^3}\Big)(x_+^2 + y_+^2) + \Big(1 - \frac{\alpha}{R^3}\Big)(x_-^2 + y_-^2) + \\ &\qquad \Big(1 - 2\frac{\alpha}{R^3}\Big)z_+^2 + \Big(1 + 2\frac{\alpha}{R^3}\Big)z_-^2\Big] \qquad (10') \end{aligned}$$

The frequencies of these six oscillators are given by

$$\begin{aligned} \nu_x^{\pm} = \nu_y^{\pm} &= \nu_0\sqrt{1 \pm \alpha/R^3} \approx \nu_0\Big(1 \pm \frac{\alpha}{2R^3} - \frac{\alpha^2}{8R^6} \pm \ldots\Big) \\ \nu_z^{\pm} &= \nu_0\sqrt{1 \mp 2\alpha/R^3} \approx \nu_0\Big(1 \mp \frac{\alpha}{R^3} - \frac{\alpha_2}{2R^6} \mp \ldots\Big) \qquad (12) \end{aligned}$$

Here $\nu_0 = \frac{e}{\sqrt{m\alpha}}$ is the *proper frequency* of the two elastic systems, if isolated from each other ($R \to \infty$), and m is their reduced mass. Assuming $\alpha \ll R^3$, we have developed the square roots in (12) into powers of (α/R^3).

The lowest state of this system of six oscillators will therefore be given, according to (11), by:

$$E_0 = \frac{h}{2}(\nu_x^+ + \nu_y^+ + \nu_z^+ + \nu_x^- + \nu_y^- + \nu_z^-)$$
$$= \frac{h\nu_0}{2}\left[6 + (\tfrac{1}{2} + \tfrac{1}{2} - 1 - \tfrac{1}{2} - \tfrac{1}{2} + 1)\frac{\alpha}{R^3} - (\tfrac{1}{2} + \tfrac{2}{2})\frac{\alpha^2}{R^6} + \ldots\right]$$
$$= 3h\nu_0 - \frac{3}{4}\frac{h\nu_0\alpha^2}{R^6} + \ldots.$$

The first term $3h\nu_0$ is, of course, simply the internal zero-point energy of the two isolated elastic systems. The second term, however,

$$U = -\frac{3}{4}\frac{h\nu_0\alpha^2}{R^6} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

depends upon the distance R and is to be considered as an interaction energy which, being negative, characterises an attractive force. We shall presume that this type of force,[4] which is not conditioned by the existence of a permanent dipole or any higher multipole, will be responsible for the Van der Waals attraction of the rare gases and also of the simple molecules H_2, N_2, etc. For reasons which will be explained presently these forces are called the *dispersion effect.*

§ 5. Dispersion Effect; General Formula.[5]

Though it is of course not possible to describe this interaction mechanism in terms of our customary classical mechanics, we may still illustrate it in a kind of semi-classical language.

If one were to take an instantaneous photograph of a molecule at any time, one would find various configurations of nuclei and electrons, showing in general dipole moments. In a spherically symmetrical rare gas molecule, as well as in our isotropic oscillators, the average over very many of such snapshots would of course give no preference for any direction. These very quickly varying dipoles, represented by the zero-point motion of a molecule, produce an electric field and act upon the polarisability of the other molecule and produce there induced dipoles, which are in phase and in interaction with the instantaneous dipoles producing them. The zero-point motion is, so to speak, accompanied by a synchronised electric alternating field, but not by a radiation field: The energy of the zero-point motion cannot be dissipated by radiation.

This image can be used for interpreting the generalisation of our formula (13) for the case of a general molecule, the exact development of which would of course need some quantum mechanical calculations.

We may imagine a molecule in a state k as represented by an orchestra of periodic dipoles μ_{kl} which correspond with the frequencies

$$\nu_{kl} = \frac{E_l - E_k}{h}$$

of (not forbidden) transitions to the states l. These "oscillator strengths," μ_{kl}, are the same quantities which appear in the "dispersion formula" which gives the polarisability $\alpha_k(\nu)$ of the molecule in the state k when acted on by an alternating field of the frequency ν.

$$\alpha_k(\nu) = \frac{2}{3h}\sum_l \frac{\mu_{kl}^2\nu_{kl}}{\nu_{kl}^2 - \nu^2}. \quad . \quad . \quad . \quad (14)$$

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[4] This type of force first appeared in a calculation of S. C. Wang, *Physik. Z.* 1927, **28**, 663.

[5] R. Eisenschitz and F. London, *Z. Physik*, 1930, **60**, 491.

If the acting field of the frequency ν_0 has the amplitude F_0, the induced moment M is given by

$$M = \alpha_k(\nu_0) \cdot F_0 = \frac{2}{3h} F_0 \sum_l \frac{\mu_{kl}^2 \nu_{kl}}{\nu_{kl}^2 - \nu_0^2} \quad . \quad . \quad (1')$$

and the interaction energy between field and molecule by

$$U = -\tfrac{1}{2}\alpha(\nu_0) \cdot F_0^2 = -\frac{F_0^2}{3h} \sum_l \frac{\mu_{kl}^2 \nu_{kl}}{\nu_{kl}^2 - \nu_0^2}. \quad . \quad . \quad (5')$$

Now this acting field may be produced by another molecule by one of its periodic dipoles $\mu_{\rho\sigma}$ with the frequency $\nu_{\rho\sigma}$ and inclination $\theta_{\rho\sigma}$ to the line joining the two molecules. Near the first molecule (we call it the "Latin" molecule, using Latin indices for its states, and Greek indices to the other one) the dipole $\mu_{\rho\sigma}$ produces an electric field of the strength (compare (6)):

$$F_{\rho\sigma} = \frac{\mu_{\rho\sigma}}{R^3} \sqrt{1 + 3\cos^2\theta_{\rho\sigma}}. \quad . \quad . \quad . \quad (6')$$

This field induces in the Latin molecule a periodic dipole of the amount:

$$M_{\rho\sigma}^k = \alpha_k(\nu_{\rho\sigma}) \cdot F_{\rho\sigma},$$

and an interaction energy (compare (5')):

$$-\frac{\alpha_k(\nu_{\rho\sigma})}{2} F_{\rho\sigma}^2 = -\frac{\mu_{\rho\sigma}^2}{3hR^6}(1 + 3\cos^2\theta_{\rho\sigma}) \sum_l \frac{\mu_{kl}^2 \nu_{kl}}{\nu_{kl}^2 - \nu_{\rho\sigma}^2}.$$

If we now consider the whole orchestra of the "Greek" molecule in the state ρ we have to sum over all states σ and to average over all directions $\theta_{\rho\sigma}$ ($\cos^2\theta = 1/3$). This would give us the action of the Greek atom upon the polarised Latin atom:

$$U_{\rho \to k} = -\frac{2}{3hR^6} \sum_{l\sigma} \frac{\mu_{kl}^2 \mu_{\rho\sigma}^2 \nu_{kl}}{\nu_{kl}^2 - \nu_{\rho\sigma}^2}.$$

Adding the corresponding expression $U_{k \to \rho}$ for the action of the Latin molecule upon the Greek one, we obtain the total interaction due to the "periodic" dipoles of a molecule in the state k with another in the state ρ:

$$U_{\rho k} = U_{\rho \to k} + U_{k \to \rho} = -\frac{2}{3hR^6} \sum_{l\sigma} \mu_{kl}^2 \mu_{\rho\sigma}^2 \left(\frac{\nu_{kl}}{\nu_{kl}^2 - \nu_{\rho\sigma}^2} + \frac{\nu_{\rho\sigma}}{\nu_{\rho\sigma}^2 - \nu_{kl}^2} \right)$$

$$= -\frac{2}{3hR^6} \sum_{l\sigma} \frac{\mu_{kl}^2 \mu_{\rho\sigma}^2}{\nu_{kl} + \nu_{\rho\sigma}} \quad . \quad . \quad . \quad . \quad (15)$$

§ 6. Additivity of the Dispersion Effect.

Of course this reasoning does not claim to be an exact proof of (15), but it may perhaps illustrate the mechanism of these forces. It can be shown that the formula (15) has the peculiarity of *additivity;*[3] this means that if three molecules act simultaneously upon each other, the three interaction potentials between the three pairs of the form (15) are simply to be added, and that any influence of a third molecule upon the interaction between the first two is only a small perturbation effect of a smaller order of magnitude than the interaction itself. These attractive forces can therefore simply be superposed according to the parallelogram of forces, and they are consequently able to *represent the fact of a general cohesion.*

If several molecules interact simultaneously with each other, one has to imagine that each molecule induces in each of the others a set of co-ordinated periodic dipoles, which are in constant phase relation with the corresponding inducing original dipoles. Every molecule is thus the seat of very many incoherently superposed sets of induced periodic dipoles caused by the different acting molecules. Each of these induced dipoles has always such an orientation that it is attracted by its corresponding generating dipole, whereas the other dipoles, which are not correlated by any phase relation, give rise to a *periodic* interaction only and, on an average over all possible phases, contribute *nothing* to the interaction energy. So one may imagine that the simultaneous interaction of many molecules can simply be built up as an *additive* superposition of single forces between pairs.

§ 7. Simplified Formula; Some Numerical Values.

For many simple gas molecules (*e.g.* the rare gases, H_2, N_2, O_2, CH_4), the empirical dispersion curve has been found to be representable, in a large frequency interval, by a dispersion formula of the type (14) consisting of one single term only. That means that for these molecules the oscillator strength μ_{kl} for frequencies of a small interval so far exceed the others that the latter can entirely be neglected. In this case, and for the limiting case $\nu \rightarrow 0$ (polarisability in a *static* field) the formula (14) can simply be written:

$$\alpha_k \equiv \alpha_k(0) = \frac{2}{3h}\frac{\mu_k^2}{\nu_k} \quad . \quad . \quad . \quad . \quad (14')$$

(μ_k signifies the dipole-strength of the only main frequency ν_k) and formula (15) for the interaction of the two systems goes over into:

$$\begin{aligned} U_{pk} &= -\frac{2}{3hR^6}\frac{\mu_k^2}{\nu_k}\cdot\frac{\mu_p^2}{\nu_p}\cdot\frac{\nu_k\cdot\nu_p}{\nu_k+\nu_p} \\ &= -\frac{3h}{2R^6}\cdot\alpha_k\alpha_p\frac{\nu_k\cdot\nu_p}{\nu_k+\nu_p} \quad . \quad . \quad . \quad (13') \end{aligned}$$

This formula is identical with (13) in the case of two molecules of the same kind. It can, of course, only be applied if one already knows that the dispersion formula has the above-mentioned special form. But in any case, if the dispersion formulæ of the molecules involved are empirically known, their data can be used and are sufficient to build up the attractive force (15). No further details of the molecular structure need be known.

We give, in Table I., a list of theoretical values for the attractive constant c (*i.e.* the factor of $-1/R^6$ in the above interaction law) for rare gases and some other simple gases where the refractive index can fairly well be represented by a dispersion formula of one term only. The characteristic frequency ν_D multiplied by h is in all these cases very nearly equal to the ionisation energy $h\nu_I$. This may, to a first approximation, justify using the latter quantity in similar cases where a dispersion formula has not yet been determined. It is seen that the values of

c vary in a ratio from 1 to 1000, and this wide range of the order of magnitude makes even a very crude experimental test of these forces instructive (see § 11).

TABLE I.—DISPERSION EFFECT BETWEEN SIMPLE MOLECULES.

	$h\nu_I$ (e. Volts).	$h\nu_D$ (e. Volts).	$\alpha \cdot 10^{24}$ [cm.^{3}].	$c \cdot 10^{48} = \frac{3}{4}\alpha^2 h\nu_0 \cdot 10^{48}$ [e. Volts . cm.^{6}.].
He .	24·5	25·5	0·20	0·77
Ne .	21·5	25·7	0·39	2·93
Ar .	15·4	17·5	1·63	34·7
Kr .	13·3	14·7	2·46	69
Xe .	11·5	12·2	4·00	146
H_2 .	16·4		0·81	8·3
N_2 .	17	17·2	1·74	38·6
O_2 .	13	14·7	1·57	27·2
CO .	14·3		1·99	42·4
CH_4	14·5		2·58	73
CO_2		15·45	2·86	94·7
Cl_2 .	18·2		4·60	288
HCl	13·7		2·63	71
HBr	13·3		3·58	128
HI .	12·7		5·4	278
Na .		2·1	29·7	960

J. E. Mayer[6] has shown that, for the negative rare-gas-like ions, one is not justified in simplifying the dispersion of the continuum by assuming one single frequency only. He used a simple analytical expression for the empirical continuous absorption and replacing the sums in (15) by integrals over these continua he gets the following list of c values for the 29 possible pairs of ions (Table II.):

Starting from a different method (variation method) and using some simplifying assumptions as to the wave functions of the atoms (products of single electronic wave functions) Slater and Kirkwood[6a] have also calculated these forces. They found the following formula:

$$U = -\frac{1}{R^6}\frac{3eh}{8\pi}\sqrt{\frac{N\alpha^3}{m}} \quad . \quad . \quad . \quad (13'')$$

(N = number of electrons in the outer shell.)

This expression usually gives a somewhat greater value than (13) and may be applied in those cases in which the characteristic frequencies in (13) are not obtainable. But at present it is difficult to say how far one *may rely on formula* (13″).

TABLE II.—DISPERSION EFFECT BETWEEN IONS.

($c \cdot 10^{48}$ in units [e . volts cm.^{6}]).

	F^-.	Cl^-.	Br^-.	I^-.		
Li^+ .	c_{-+} = 0·13	3·2	4·0	5·4	c_{++}	0·11
Na^+ .	7·14	17·8	22·2	30·3		2·68
K^+ .	31·0	76·3	95·3	130		38·6
Rb^+ .	49·2	125	157	214		94·3
Cs^+ .	82·5	205	259	356		247
	c_{--} = 23-30	176-206	294-332	600-670		

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[6] J. E. Mayer, *J. Chem. Physics*, 1933, **1**, 270.

[6a] J. C. Slater and J. G. Kirkwood, *Physic. Rev.*, 1931, **37**, 682.

§ 8. Systematics of the Long Range Forces.[7]

The formula (15) applies quite generally for freely movable molecules so long as the interaction energy can be considered as small compared with the separation of the energy-levels of the molecules in question; *i.e.* so long as

$$\frac{\mu_{kl}\mu_{\rho\sigma}}{R^3} < | E_k - E_l + E_\rho - E_\sigma | \quad . \quad . \quad (16)$$

With this restriction, the formula (15) holds for freely movable dipole molecules, as well as for rare gas molecules. There is therefore always a minimum distance for R up to which we can rely on (15).

The difference between a molecule with permanent dipole and a rare gas molecule consists in the following: A rare gas molecule has such a high excitation energy (electronic jump) that for normal temperatures we can assume that all molecules are in the ground state; therefore we have forces there independent of temperature. For a dipole molecule, on the other hand, we have to consider a Boltzmann distribution over at least the different rotation states, because the energy difference between these states is usually small in comparison with kT.

Let us at first consider an ***absolutely rigid dipole*** (dumb-bell) molecule (*i.e.* a molecule without electronic or oscillation states). Then the probability $p_{\rho k}$ that the Greek molecule is in the pure rotation state ρ and the Latin one in the pure rotation state k is given by

$$p_{\rho k} = Ae^{-\frac{1}{kT}(E_k + E_\rho)}$$

where

$$A^{-1} = \sum_{k\rho} e^{-\frac{1}{kT}(E_k + E_\rho)}.$$

The mean interaction between two such molecules is accordingly

$$\bar{U} = \sum_{\rho k} p_{\rho k} U_{\rho k} = -\frac{2A}{3R^6} \cdot \sum_{\sigma l} \frac{\mu_{kl}{}^2 \mu_{\rho\sigma}{}^2}{E_l - E_k + E_\sigma - E_\rho} e^{-\frac{E_k + E_\rho}{kT}}. \quad (17)$$

If in this expression we interchange the notation of the summation indices ρ and k with σ and l, the value of the sum of course remains unchanged. Therefore, taking the average of these two equivalent expressions we can write (since $\mu_{kl} = \mu_{lk}$):

$$\bar{U} = -\frac{A}{3R^6} \sum_{\substack{\sigma l \\ \rho k}} \mu_{kl}{}^2 \mu_{\rho\sigma}{}^2 \frac{e^{-\frac{E_k + E_\rho}{kT}} - e^{-\frac{E_l + E_\sigma}{kT}}}{E_l + E_\sigma - E_k - E_\rho}. \quad . \quad (17')$$

Developing the exponentials into powers of $1/kT$ we notice that the constant terms cancel each other (no interaction for high temperature as in § 1). The first and the only important term of the development of (17') yields:

$$\bar{U} = -\frac{A}{3R^6} \frac{1}{kT} \sum_{\substack{kl \\ \rho\sigma}} \mu_{kl}{}^2 \mu_{\rho\sigma}{}^2 + \ldots = -\frac{2\mu_{\mathrm{I}}{}^2 \mu_{\mathrm{II}}{}^2}{3kTR^6} + \ldots \quad . \quad (18)$$

Here we designate by μ_{I} and μ_{II} the permanent moments of the dipole molecule, which for an absolutely rigid molecule are of course independent of the state. We therefore obtain exactly the same result as Keesom did from classical mechanics. One can, by the way, show that whilst the validity of (15) is bounded by the condition (16) the result (18) is only bounded by the weaker condition

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[7] F. London, *Z. Physik*, 1930, 63, 245.

$$\frac{\mu_{\mathrm{I}}\mu_{\mathrm{II}}}{R^3} < kT$$

which was also the limit for the validity of the classical calculation.

In reality a dipole molecule cannot, of course, be treated as a simple rigid dumb-bell. It has *electronic* and *oscillation* transitions as well. Let us, for sake of simplicity, assume that kT is big in comparison to the energy differences for pure rotation jumps, but small for all the other jumps.

In this general case we have again formula (17), but here it is sufficient to extend the Boltzmann sum $\sum\limits_{\rho k}$ only over those states which imply pure rotation jumps from the ground state, since the thermo-dynamical probability of the other states being occupied is negligible. We now divide the sum over σ and l in (17) into four parts

$$\bar{U} = U_{rr} + U_{rg} + U_{gr} + U_{gg}$$

in the following way:

(1) In U_{rr} both, σ and l, shall be restricted to those values which differ from the ground-state only by a pure rotation transition. For this sum (with certain uninteresting reservations) the above calculation for the rigid dipoles remains valid. Accordingly we get (18)

$$U_{rr} = -\frac{2}{3R^6}\frac{\mu_{\mathrm{I}}^2\mu_{\mathrm{II}}^2}{kT},$$

i.e. Keesom's orientation effect.

(2) In U_{rg} the summation over σ as before shall be extended only over those terms which differ from the ground state by a pure rotation jump; but l shall designate a great (not a pure rotation-) jump. Then we may neglect $E_\sigma - E_\rho$ in comparison with $E_l - E_k$ in the denominators of (17) and can write

$$U_{rg} = -\frac{2A}{3R^6}\left(\sum_{kl}\mu_{kl}^2 e^{-\frac{E_k}{kT}}\right)\cdot\left(\sum_{\rho\sigma}\frac{\mu_{\rho\sigma}^2}{E_\sigma - E_\rho}e^{-\frac{E_\rho}{kT}}\right).$$

Comparison with (14) shows that the terms of the second sum on the right-hand side can be represented by the static polarisability $\alpha_\rho \quad \alpha_\rho(o)$ of the second molecule which will depend very little on the state of rotation ρ of the molecule so that we may signify it simply by α_{II}; whereas the first sum again gives the square of the permanent dipole moment of the first molecule, of which we also may assume that it is approximately independent of the state of rotation We obtain

$$U_{rg} = -\frac{2}{3R^6}\cdot\mu_{\mathrm{I}}^2\cdot\tfrac{3}{2}\alpha_{\mathrm{II}}(o) = -\frac{\mu_{\mathrm{I}}^2\alpha_{\mathrm{II}}}{R^6}.$$

(3) Correspondingly

$$U_{gr} = -\frac{\mu_{\mathrm{II}}^2\alpha_{\mathrm{I}}}{R^6}$$

(2) and (3) are exactly *Debye's induction effect.*

(4) In U_{gg} finally both, σ and l, shall differ from the ground state by a great (not a pure rotation-) jump. If we assume that the transition

probabilities of such a jump do not depend noticeably on the state of rotation, we can take simply the ground state for ρ and k and obtain

$$U_{gg} = -\frac{2}{3hR^6}\sum_{l\sigma}\frac{\mu_{ol}^2\mu_{o\sigma}^2}{\nu_{ol}+\nu_{o\sigma}}.$$

i.e. the *dispersion effect.* If the conditions for (13′) are fulfilled we may join the three effects in the form

$$\bar{U} = -\frac{1}{R^6}\left(\frac{2}{3}\frac{\mu_{\rm I}^2\mu_{\rm II}^2}{kT} + \mu_{\rm I}^2\alpha_{\rm II} + \mu_{\rm II}^2\alpha_{\rm I} + \frac{3h}{2}\alpha_{\rm I}\alpha_{\rm II}\frac{\nu_{\rm I}\nu_{\rm II}}{\nu_{\rm I}+\nu_{\rm II}}\right) \qquad (19)$$

We give, in Table III., a short list for the three effects of some dipole molecules :

TABLE III.—THE THREE CONSTITUENTS OF THE VAN DER WAALS' FORCES.

	$\mu \cdot 10^{18}$.	$\alpha \cdot 10^{24}$.	$h\nu_0$ (Volts).	Orientation Effect $\frac{2}{3}\frac{\mu^4}{k\,293^\circ}\cdot 10^{60}$ [erg cm.^{6}].	Induction Effect $2\mu^2\alpha \cdot 10^{60}$ [erg cm.^{6}].	Dispersion Effect $\frac{3}{4}\alpha^2 h\nu_0 \cdot 10^{60}$ [erg cm.^{6}].
CO .	0·12	1·99	14·3	0·0034	0·057	67·5
HI .	0·38	5·4	12	0·35	1·68	382
HBr .	0·78	3·58	13·3	6·2	4·05	176
HCl .	1·03	2·63	13·7	18·6	5·4	105
NH_3	1·5	2·21	16	84	10	93
H_2O .	1·84	1·48	18	190	10	47

It is seen that the induction effect is in all cases practically negligible, and that even in such a strong dipole molecule as HCl the permanent dipole moments give no noticeable contribution to the Van der Waals' attraction. Not earlier than with NH_3 does the orientation effect become comparable with the dispersion effect, which latter seems in no case to be negligible.

§ 9. Limits of Validity.

We have yet to discuss the physical meaning of the condition (16).

In quantum mechanics, in characteristic contrast to classical mechanics, a freely movable polyatomic molecule has a centrally symmetric and, particularly in its lowest state, a spherically symmetric structure, *i.e.* a spherically symmetric probability function. That means that on the average, even in its lowest state, a free molecule does not prefer any direction, it changes its orientation permanently owing to its zero-point motion. If another molecule tries to orientate the molecule in question a compromise between the zero-point motion and the directing power will be made, but only for

$$\frac{\mu_{\rm I}\mu_{\rm II}}{R^3} > |E_0 - E_1| \quad . \quad . \quad . \quad . \quad (20a)$$

the directive forces preponderate over the zero-point rotation. Accordingly, in this case, the motion of the dipoles becomes more similar to a vibration near the equilibrium orientation of the dipoles (parallel to each other along the line joining the two molecules) and the interaction will then be of the nature of orientated dipoles, *i.e.* of the order of magnitude of

$$-\frac{2\mu_{\rm I}\mu_{\rm II}}{R^3}.$$

In quantum mechanics, we learn, in contrast to (3), the condition

$$\frac{\mu_{\mathrm{I}}\mu_{\mathrm{II}}}{R^3} > kT \quad . \quad . \quad . \quad . \quad (20b)$$

is not sufficient for the molecules being orientated. The orientating forces have not only to overcome the temperature motion but in addition the zero-point motion also. If Θ is the moment of inertia of the molecule the right-hand side of (20*a*) becomes equal to $\frac{h^2}{4\pi\Theta}$; and using this one can easily show that, for example, for HI molecules, at the distances they have in the solid state, the directive forces of the dipoles are still too weak to overcome the zero-point rotation. One has therefore to imagine these molecules always rotating even at the absolute zero in the solid state. But HI is certainly rather an exceptional case.

It is obvious that for larger molecules and for small molecular distances in the solid and liquid state the directive forces are quite insufficiently represented by the dipole action. For these one has simply to replace the left-hand side of (20) by the classical orientation energy in order to obtain a reasonable estimate for the limit of free motion.

As long as we are within the limits of (16) our argument in § 6 as to the additivity holds quite generally for all the three effects collected in formula (19). Only if, in consequence of (20), the free motion of the molecules is hampered does the criticism of § 3 apply, and this concerns the non-additivity of the direction effect as well as of the induction effect.

The internal *electronic* motion of a molecule, however, will not appreciably be influenced when the rotation of the molecule as a whole is stopped. Thus one is justified in applying the formula for the dispersion effect for non-rotating molecules also.

It is obvious, however, that only the highly compact molecules, as listed in Tables I. and II., can reasonably be treated simply as force centres. For the long organic molecules it seems desirable to try to build up the Van der Waals' attraction as a sum of single actions of parts of the molecules. As it is rather arbitrary to attribute the frequencies appearing in (15) or (13) to the single parts of a molecule, it has been attempted[8] to eliminate them by making use of the approximate additivity of the atomic refraction as well as of the diamagnetic susceptibility.

If there is one single "strong" oscillator μ_k only (*cf.* 14′) the diamagnetic susceptibility has simply the form:

$$\chi_k = -\frac{\mu_k{}^2 N_L}{6mc^2}\,(< 0) \quad (N_L \text{ Loschmidt's number})$$

therefore, because of (14′),

$$\nu_k = \frac{2}{3h}\frac{\mu_k{}^2}{\alpha_k} = \frac{4mc^2}{hN_L}\frac{\chi_k}{\alpha_k}.$$

We can therefore write, instead of (13′),

$$U_{k\rho} = \frac{3}{2}\frac{h}{R^6}\alpha_k\alpha_\rho\frac{4mc^2}{hN_L}\frac{\frac{\chi_k}{\alpha_k}\frac{\chi_\rho}{\alpha_\rho}}{\chi_k/\alpha_k + \chi_\rho/\alpha_\rho}$$

$$= \frac{1}{\mathrm{R}^6}\frac{6mc^2}{N_L}\frac{\alpha_k\alpha_\rho}{\alpha_k/\chi_k + \alpha_\rho/\chi_\rho} \quad . \quad . \quad . \quad (13'')$$

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[8] J. G. Kirkwood, *Physik. Z.*, 1932, **33**, 57; A. Müller, *Proc. Roy. Soc. A*, 1936, **154**, 624.

In this formula the interaction energy is represented by approximately additive atomic constants, and it seems quite plausible to build up in such a way the Van der Waals' attraction of polyatomic molecules from single atomic actions. But the comparison given in Table IV. shows that the exactitude of this method is apparently not very great.

TABLE IV.

	$\frac{3mc^2}{N_L}\alpha\chi \cdot 10^{48}$.	$\cdot 10^{60}$ (Table I.).
He	0·84	0·77
Ne	4·94	2·93
A	69·0	34·7
Kr	180	69
X	448	146

For the *dispersion effect* also, the condition (16) indicates a characteristic limit. The quantity $\frac{\mu^2_{kl}}{E_k - E_l}$ is practically identical with the polarisability α, if $E_k \to E_l$ is the "main" electronic jump (compare 14′). Accordingly, instead of (16) we may roughly write

$$\alpha < R^3 \quad . \quad . \quad . \quad . \quad (16')$$

as condition for the validity of our formulæ for the dispersion effect. What $\alpha > R^3$ would mean can easily be inferred from considering our simple model (§ 4): Some of the proper frequencies (12) would become imaginary, and that indicates that for these short distances the rest positions of the electrons would no longer be positions of stable equilibrium.

Some time ago Herzfeld [9] noticed that if R_0 is the shortest possible atomic distance (atomic diameter) the alternative "$\alpha > R_0^3$ or $\alpha < R_0^3$" nearly coincides with the alternative "*metal* or *insulator*." Accordingly, for the non-metallic atoms and molecules listed in Table I. one is always within the limits of (16).

§ 10. Higher Approximations. Repulsive Forces.

The formula (15) is very far from completely representing the molecular forces, even of the rare gases, for all distances. It can be considered as a first step of a calculus of successive approximation. The state of a molecule is of course only quite roughly characterised by its orchestra of periodic dipoles; there are obviously also periodic quadrupoles and higher multipoles, which give rise to similar interactions proportional to R^{-8}, R^{-10}, etc. For big distances these terms are in any case smaller than the R^{-6} forces, and there one may rely on formula (15). For He and H-atoms one [10] could calculate the R^{-8} term and could show that for small distances it can give rise to a contribution comparable with the R^{-6} term. But the R^{-10} term seems always to be negligible.

For these small distances, however, quite another effect has also to be considered. Even if a molecule does not show any permanent multipole but has, on an average, an absolutely spherically symmetrical structure, *e.g.* like the rare gases, quite apart from all effects due to the internal electronic motion, the mean charge distribution itself gives rise to a strong, so to speak "static," interaction, simply owing to the fact that by penetrating each other the electronic clouds of two molecules no longer screen the nuclear charges completely and the nuclei repel each other by the electrostatic Coulomb forces. In addition to this, and simultaneously, a second influence is to be considered. Already the penetration of the two electronic clouds is hampered by the Pauli Principle: two electrons can only be in the same volume element of space if they have sufficiently *different velocity*. This means that for the reciprocal penetration of the two clouds of electrons the velocity and therefore also the kinetic energy of the internal electronic motion must be augmented: energy must be supplied with the approach of the molecules, *i.e.* repulsion.

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[9] K. F. Herzfeld, *Physic. Rev.*, 1927, 29, 701.

[10] H. Margenau, *ibid.*, 1931, 38, 747.

This repulsion corresponds to the *homopolar attraction* in the case of unsaturated molecules. In an unsaturated molecule there are electrons with unsaturated spin and of these, when penetrating the cloud of a corresponding other molecule, the Pauli Principle no longer demands "sufficiently different" velocity but *only different spin orientation*. In that case, consequently, one has a repulsion only for much smaller distances.

The actual calculation of the repulsive forces needs of course a very exact knowledge of the charge distribution on the surface of the molecules, and therefore presents considerable difficulties; hitherto, a detailed calculation could only be carried out for the very simplest case[11] of He. The most successful attempts[12] in this direction so far have applied the ingenious Thomas-Fermi method which takes the Pauli Principle directly as a basis and is accordingly able, neglecting many unessential details, to account for just that effect which is characteristic of this penetration mechanism.

It is impossible here to reproduce the results of these numerical methods. Up to now the repulsive forces have been successfully calculated only for the interaction between the rare gas-like ions, not yet for the rare gases themselves. This is not because the repulsive forces between the neutral rare gas molecules constitute a very different problem, but because a considerably smaller degree of exactitude of the repulsive forces gives a useful description, when they are balanced by the strong ionic attractive forces instead of the weak molecular forces only.

The chemist at present must be satisfied with the knowledge that the repulsive forces depend on rather subtle details of the charge distribution of the molecules, and that consequently there is no reason to hope that one might connect them with other simple constants of the molecules, as is possible for the far-reaching attractive forces. Their theoretical determination is in any special case another problem of pure numerical calculations. But what really will interest the chemist is the fact that it can generally be shown that these homopolar repulsive forces (in characteristic contrast with the above-mentioned homopolar binding forces) have also the property of additivity, in the same approximate sense as the R^{-6} forces are additive, and that, therefore, to a first approximation, it will be quite justified to assume for the repulsive forces also simple analytical expressions, to superpose them simply additively and so to try to determine them from empirical data of the liquid or solid state. Whereas formerly one used to presume a power-law of the form b/R^n for these repulsive forces, quantum mechanics now shows that an exponential law of the form

$$be^{-R/\rho}$$

gives a more appropriate representation of the repulsion.

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[11] J. C. Slater, *Physic. Rev.*, 1928, 32, 349; see also W. E. Bleand J. E. Mayer, *Journ. chem. Physics*, 1934, 2, 252.

[12] H. Jensen, *Z. Physik.*, 1936, 101, 164; P. Gombar, *ibid.*, 1935, 93, 378.

In this form one now usually presumes the repulsive forces and determines the constants b and ρ empirically.

For the attraction one uses the expression (15) or (13) possibly completed by a term proportional to R^{-8}. The factor R^{-8} supplies a third constant which also has to be empirically determined. For rare-gas like ions of the charges e_1, e_2, finally, one has of course to add the Coulombian term $+\frac{e_1 e_2}{R}$.

Thus, altogether one usually now takes, for the simplest molecules, an expression of the form

$$U = be^{-R/\rho} - c/R^6 - d/R^8 + \frac{e_1 e_2}{R} \quad . \quad . \quad . \quad (21)$$

as a reasonable basis, where b, ρ, d are adjustable parameters, whereas c, e_1, e_2 are regarded as theoretically given. Thus, in all applications of the Van der Waals' forces a considerable freedom remains, and this is to be noticed when one wishes to test the theory.

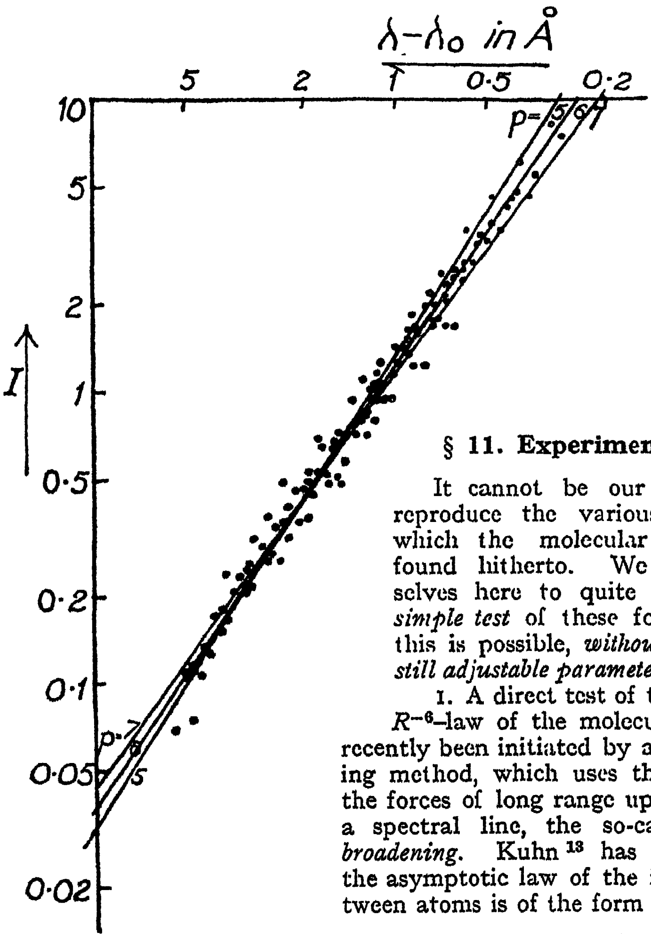

FIG. 1.—Intensity distribution and molecular forces.

§ 11. Experimental Test.

It cannot be our task here to reproduce the various applications which the molecular forces have found hitherto. We confine ourselves here to quite a rough and *simple test* of these forces so far as this is possible, *without adapting the still adjustable parameters* in (21).

1. A direct test of the asymptotic R^{-6}-law of the molecular forces has recently been initiated by a very interesting method, which uses the influence of the forces of long range upon the form of a spectral line, the so-called *pressure-broadening*. Kuhn[13] has shown that if the asymptotic law of the interaction between atoms is of the form

$$U \approx \frac{c}{R^p}$$

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[13] H. Kuhn, *Phil. Mag.*, 1934, 18, 987; *Proc. Roy. Soc. A*, 1936 *in print;* see also H. Kuhn and F. London, *Phil. Mag.*, 1934, 18, 983.

the intensity in a certain region of the spectral line is given by

$$\mathrm{I}(\nu) = \frac{k}{(\nu_0 - \nu)^{\frac{p+3}{p}}}.$$

Thus the inclination of log (I) as a function of log ν gives immediately the exponent p. Thereupon Minkowski[14] has discussed his measurements of the broadening of the D-lines of Na by Argon. He gives the following figure of his measured values of log (I) (Fig. 1). In addition, we have drawn the lines corresponding to $p = 5$, $p = 6$ and $p = 7$. One sees that the accuracy of the measurements does not yet permit an exact determination of p. But in any case we may say that $p = 6$ fits much better than $p = 5$ or $p = 7$, and that $p = 8$ and $p = 4$ can be excluded with certainty.

2. Testing the theory by the *gas equation* we shall restrict ourselves here to a quite rough check by means of the Van der Waals' a and b only. If this test has a satisfactory result, the exact dependence of the second virial coefficient on temperature may be used for determining *backwards* the still adjustable parameters in (21). But since it is always possible to get a fairly good agreement with the second virial coefficient by adjusting an expression like (21) it seems desirable to simplify the situation in such a way that, if possible, no adjustable parameters would be involved.

Accordingly, we replace (21) by:

$$U = \begin{cases} -\,c/R^6 \text{ for } R \geqq R_0 \\ +\,\infty \text{ for } R < R_0 \end{cases} \qquad . \quad . \quad . \quad (22)$$

That means we idealise the molecules as infinitely impenetrable spheres, and neglect for $R > R_0$ the two adjustable terms $be^{-R/\rho}$ and $-\,d/R^8$ entirely. For large values of R the term $-\,c/R^6$ is certainly the only noticeable one. For mean distances $R \gtrsim R_0$ the two neglected terms, having different sign, may to a large extent cancel each other. For $R < R_0$ the very sudden increase of the exponential repulsion is replaced by an infinitely sudden one. By this procedure the order of magnitude of the minimum of U may be affected by a common factor, but will not be completely mutilated. Instead of the three adjustable parameters of (21) we have now only one: the size R_0.

The second virial coefficient B_2 is defined by the development of the gas equation into powers of $\frac{1}{V}$.

$$\frac{pV}{N_L kT} = 1 + \frac{B_2(T)}{V} + \frac{B_3(T)}{V^2} + \ldots,$$

and is given theoretically by

$$B_2 = 2\pi N_L \int_0^\infty \left(1 - e^{-\frac{U}{kT}}\right) r^2 \, \mathrm{d}r \qquad . \quad . \quad . \quad (23)$$

In the development of B_2 into powers of $\frac{1}{T}$, the first two terms can be identified with the corresponding terms of Van der Waals' equation:

$$\frac{pV}{N_L kT} = \frac{V}{V-b} - \frac{a}{VN_L kT} \approx 1 + \frac{1}{V}\left(b - \frac{a}{N_L kT}\right) + \frac{1}{V^2}(\ldots) + \ldots$$

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[14] R. Minkowski, *Z. Physik*, 1935, **93**, 731.

The comparison gives:

$$B_2 = b - \frac{a}{N_L kT} + \ldots,$$

and if we now substitute (22) into (23) and consider that for high temperatures $U \gg - kT$ for all values of R, we obtain:

$$b = \frac{2\pi N_L R_0^3}{3}$$

$$a = - 2\pi N_L^2 \int_{R_0}^{\infty} U R^2 dR = \frac{2\pi N_L^2 c}{3 R_0^3}.$$

In these two equations we may eliminate R_0^3 and obtain:

$$ab = \frac{4\pi^2 N_L^3}{9} . c = 1 . 51 \times 10^{54} . c \qquad . \qquad . \quad (24)$$

Here the numerical factor is so determined that a, as usual, is measured in [atm. cm.^{6} g.$^{-2}$] and c in the units of Table I.

If b is taken from the experimental gas equation the relation (24) can be used for predicting the constant a. These values are listed as $a_{\text{theor.}}$ in Table V., where they can be compared with the experimental values $a_{\text{exp.}}$

TABLE V.—VAN DER WAALS a-CONSTANT AND HEAT OF SUBLIMATION.

	$b_{\text{exp.}}$ [cm^3].	$a_{\text{theor.}} \cdot 10^{-4}$ [atm. cm.^{6}g^{-2}].	$a_{\text{exp.}} \cdot 10^{-4}$ [atm. cm.^{6}g^{-2}].	ρ.	$L_{\text{theor.}} \cdot 10^{-3}\ \frac{\text{cal.}}{\text{mol.}}$	$L_{\text{exp.}} \cdot 10^{-3}\ \frac{\text{cal.}}{\text{mol.}}$
He .	24	4·8	3·5			
Ne .	17	26	21	1·46	0·47	0·59
Ar .	32·3	163	135	1·70	1·92	2·03
Kr .	39·8	253	240	3·2	3·17	2·80
Xe .	51·5	430	410			
H_2 .	26·5	46	24·5			
N_2 .	39·6	147	135	1·03	1·64	1·86
O_2 .	31·9	135	136	1·43	1·69	2·06
CO .	38·6	166	144	1·05	1·86	2·09
CH_4 .	42·7	256	224	0·53	2·42	2·70
CO_2 .	42·8	334	361			
Cl_2 .	54·8	680	632	2·00	7·18	7·43
HCl .	40·1	283	366	1·56	3·94	5·05
HBr .	44·2	510	442	2·73	4·45	5·52
HI .				3·58	6·65	6·21

It is needless to say how inadequate the use of the critical data is for determining the limiting values for $T \rightarrow \infty$ of the second virial coefficient. These inadequacies may produce an uncertainty of perhaps 30 per cent., and our simplified expression (22) may also introduce an error of such an order of magnitude. But these uncertainties will presumably give rise only to a common systematic error for all molecules considered, and though the good absolute agreement found in the list is to be regarded as a lucky chance the relative agreement between theoretical and experimental a-values over such a wide range is certainly not disputable. That may justify trying to improve our knowledge of the Van der Waals forces by adjusting the expression (21) by means of the empirical second virial coefficient. Hitherto this has only been tried[15] by adding a law of the form b/R^n for the repulsion. But this procedure inevitably gives too small a molecule size, as it must attribute to the R^{-6}–forces what is due to the neglect of the R^{-8}–forces and of the sudden decrease of the exponential repulsion.

3. In Table V. is also listed the *lattice energy* L (sublimation heat extrapolated to absolute zero after subtraction of the zero-point energy) for some molecule lattices, calculated on the basis of the same simplified formula (22). In all cases we have assumed closest packed structure, as this structure is at least approximately realised in the molecular lattices in question. The summation of (22) over the lattice gives

$$L = 8{\cdot}36 \, . \, N_L^2 \frac{c}{v^2} 10^4 \left[\frac{\text{cal}}{\text{mol}}\right] = 3{\cdot}04 \times 10^{52} \frac{c \, . \, \rho^2}{M^2} \left[\frac{\text{cal}}{\text{mol}}\right] . \quad . \quad (25)$$

Here c is to be taken from Table I., v is the experimental mol. volume, ρ = density, M = molecular weight.

This test is instructive in so far as it shows plainly the additivity of the forces, and particularly the increase of L from HCl to HI with decreasing dipole moments clearly demonstrates the preponderance of those forces which are not due to the permanent moments.*

When the full expression (21) will be determined, say, from the experimental second virial coefficient it will be possible to calculate all constants (compressibility, elastic constants, etc.) of these molecular lattices.

For the constitution of the *ionic* lattices also, the Van der Waals attraction has been found to be a very decisive factor. We know the forces at present much better for these ions than for the neutral molecules. Using an interaction of the form (21), Born and Mayer[16] have calculated the lattice energy of all alkali halides for the NaCl-type and simultaneously for the CsCl-type and comparing the stability of the two types they could show quantitatively that the relatively great Van der Waals attraction between the heavy ions Cs^+, I^-, Br^-, Cl^- (*cf.* Table II.) accounts for the fact that CsCl, CsBr, CsI, and *these only*, prefer a lattice structure in which the ions of the same kind have smaller distances from each other than in the NaCl-type. The contribution of the Van der Waals' forces to the total lattice energy of an ionic lattice is of course a relatively small one, it varies from 1 per cent. to 5 per cent., but just this little amount is quite sufficient to explain the transition from the NaCl-type to the CsCl-type.

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[15] K. Wohl, *Z. physik. Chem. B*, 1931, **41**, 36; J. E. Lennard-Jones, *Proc. Physic. Soc.*, 1931, **43**, 461.

* In Table V. the lattice energies of He and H_2 have been omitted, because in these lattices the zero-point energy of the nuclear motion gives such a great contribution that it cannot be neglected. Therefore H_2 and He cannot immediately be compared with the other substances. See F. London, *Proc. Roy. Soc. A*, 1936, **153**, 576.

[16] M. Born and J. E. Mayer, *Z. Physik*, 1932, **75**, J. E. Mayer, *J. Chem. Physics*, 1933, **1**, 270.

AN ATTEMPT AT A MOLECULAR THEORY OF LIQUID STRUCTURE.

By J. D. Bernal.

Received 3rd September, 1936.

In recent years there has been a very considerable advance in our knowledge of the molecular arrangements in liquids. X-ray investigations in particular have furnished evidence as to the mutual arrangements of atoms and molecules in a number of different liquids. The work, however, has been on the whole descriptive, and the wider problems of why the liquid state should exist at all and why the internal constitutions of different liquids should differ, have as yet only been touched.

The two main characteristics of the liquid state from the molecular point of view are its coherence and its fluidity, which in turn depends on the irregularity of distribution of its component atoms or molecules and the capacity of those distributions to change under the influence of heat or the mechanical stress. In attempting any theory of these effects, it is best at the outset to impose certain limitations. In the first place, only monatomic or quasi-monatomic liquids will be dealt with, such as those of the metals, the rare gases, and such compounds as methane or nitrogen. The effects of the shape of molecules and of the presence of active association centres make the theory of organic liquids or of water extremely difficult as a first step, though suggestions of a qualitative theory of these liquids are given later. A second equally fundamental restriction is the assumption that liquids at ordinary temperatures and pressures, *i.e.* not near to the critical point, are molecularly homogeneous, *i.e.* that they contain neither large fluctuations of density nor large regions of regular quasi-crystalline structure separated by others of completely gaseous disorder. The second assumption is one which might be disputed. The cybotactic hypothesis of such aggregations has, in fact, been put forward to explain X-ray diffraction phenomena. But the liquids on which these hypotheses were based were all of a complex organic kind where such aggregations are, indeed, likely, while there is no positive evidence that they are to be found in simple liquids. The significance of the second assumption is that around every molecule of the liquid the arrangements of other molecules are statistically equivalent; or, put in another way, *the probability of finding a molecule at a given distance from another molecule is independent of the position of either of them in the liquid.*

This leads at once to the most useful method of characterising internal configuration of a liquid. The distribution function $g(r)$ is a measure of the statistical density of molecules at a distance r from any given molecule. $4\pi r^2 g(r)\mathrm{d}r$ is hence the probability of finding a molecule within a distance r to $r + \mathrm{d}r$ of a given molecule. The distribution function of a simple liquid is indirectly derivable from its X-ray scattering curve by means of Prins' equation :—[1]

$$G(s) = \int_0^\infty 4\pi r^2 g(r) \frac{\sin (sr)}{sr} \mathrm{d}r \quad . \quad . \quad . \quad (1)$$

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[1] J. A. Prins, *Z. Physik,* 1929, 56, 617.

where G is the fraction of incident X-rays of wave-length λ scattered at an angle θ and $s = \pi \frac{\sin \theta/2}{\lambda}$.

The distribution function uniquely characterises the molecular configuration of a liquid. As it stands, however, it is an empirical and not an analytic function, and does not lend itself readily to theoretical treatment. A great simplification however has recently been introduced by Prins.[2] Making use of the long observed fact that the scattering curve of a liquid is, so to speak, a blurred copy of that of the corresponding crystalline solid, he has constructed theoretical distribution functions for liquids corresponding to different crystalline solids by allowing the integral number of molecules $n_1, n_2, n_3 \ldots$ at fixed intermolecular distances $r_1, r_2, r_3 \ldots$, characteristic of the particular crystalline state, to be varied by an error function such that $g(r)$ becomes

$$g(r) = \sum g_k(r) = \sum_k \frac{n_k}{4\pi r_k{}^2}\sqrt{\frac{a^2}{2\pi K r_k kT}}\, e^{-\frac{a^2(r-r_k)^2}{2Kr_k kT}} \quad . \quad . \quad (2)$$

where n_k, r_k are coefficients depending only on the type of crystal structure, a is a constant characteristic of the physical nature of the liquid, and K is the compressibility. In this way, Prins has shown how, to every principal type of crystal structure, there corresponds a liquid configuration, and how the distribution functions obtained for these give X-ray scattering curves agreeing well with those obtained experimentally

A still more general treatment is, however, possible if we imagine a distribution function made up of a number of maxima corresponding to the successive co-ordination spheres imagined to exist round every molecule. We have at first sight three sets of variables, the position of the maxima, their areas, *i.e.* the number of molecules in the nth co-ordination sphere, and the breadths of the peaks, *i.e.* the irregularity of the distribution in each sphere. Prins has, as a first approximation, accepted the value of the first two sets as those occurring in the crystals. Such an assumption, however, imposes unnecessary restrictions. There is no evidence that sharply distinguishable liquids of different integral co-ordination numbers exist and the absence of any true liquids with different phases at different temperatures suggests that not only do the radii of the co-ordination spheres but the numbers of molecules in them form a continuum stretching from the most closely packed liquids of 14 to 12 to those expanded liquids such as helium with co-ordination four.

Before we can profitably discuss the distribution functions of actual liquids it is necessary to consider the purely geometrical problem of the characterisation of the continuum of configurations in terms of the minimum number of variables. This presents a difficult problem in the little-known field of statistical solid geometry. The present paper contains what is merely a first attempt at a solution by intuitive and semi-empirical means. As a first step we can safely assume that the whole distribution function can be derived from that of the nearest neighbours of any point. The geometrical problem can then be stated thus. What is the distribution function of an aggregate of points in which any point is, on the average, surrounded by N others at a mean distance r_1 and at actual distances distributed according to the probability relation

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[2] J. A. Prins, *Physica*, III., 1936, 3, 147.

$$g_1(r) = \frac{N}{4\pi r_1^2}\sqrt{\frac{1}{\pi\lambda^2 r_1}}\, e^{-\frac{1}{\lambda^2}\left(\frac{r-r_1}{r_1}\right)} \qquad . \qquad . \quad (3)$$

The factors before the exponential are normalising factors and are only exactly correct when λ^2 is small.

Though the most convenient expression for geometrical treatment (3) still does not adequately represent the distribution of molecular centres of real liquids. From the unsymmetrical shape of interatomic potential functions it is clear that the distribution in the first sphere will not be a simple error function, but will be markedly skew. The number of centres on the inside of the first sphere will fall off more rapidly than on the outside, and there will be a considerable volume containing no centre.

This variation applies to the first co-ordination sphere only, and may be conveniently represented by multiplying the distribution function $g(r)$ by a factor to get the corrected function $g_c(r)$:—

$$g_c(r) = \frac{1}{2}\left\{\frac{2}{\sqrt{\pi}}\int_0^r e^{-k(r-r'_1)^2}\mathrm{d}r + 1\right\}g(r) = \Gamma_{(r)}g(r) \quad . \qquad . \quad (3')$$

where k is a factor depending on the atomic compressibility and r'_1 is a distance slightly less than r_1. The effect of such a multiplying factor is that for $r \leqslant r_1$ $g_c(r) = 0$, while for $r \geqslant r_1$ $g_c(r) = g(r)$. (Strictly the normalising factors for $g(r)$ requires a slight alteration for (3′).) In the extreme case of incompressible spheres $k = \infty$ and the multiplying factor is 0 for $r < r'_1$ and 1 for $r > r'_1$; r'_1 is here the minimum distance of approach. Except for calculations of potential energy, where closest neighbours contribute most, the simpler expression (3) is used instead of the more accurate (3′).

This restriction of closeness of approach is formally equivalent for the liquid state to those that impose symmetry conditions, *e.g.* the non-existence of five-fold axes, in the crystalline state.

* The method I used in the paper for defining the nearest neighbours of a molecule is somewhat arbitrary. But it is difficult to arrive at a geometrical definition that will be amenable to physical computations. It has been suggested to me that a topological approach might be useful. We could define as nearest neighbours, in this general way, by drawing planes bisecting the lines between all molecules and a given molecule. All those planes forming part of the smallest polyhedron around that molecule might be considered to belong to its nearest neighbours. By simple topological theory however, in this case, whatever the configuration, the average number of nearest neighbours would always be fourteen, and this would be difficult to fit into a quantitative theory. On the other hand, we might narrow down the definition by adding as a necessary condition that for molecules to count as neighbours, the mid-point of the line joining them to the origin must lie inside the smallest polyhedron. This would reduce the number of neighbours to something more approximating to the empirical definition, *i.e.*, a pseudotetrahedral co-ordination would on this definition have four neighbours on the average and not fourteen. It would still be possible however for the distance of nearest neighbours to vary widely from one another, and therefore it is not certain if much would be gained quantitatively from such a definition.

I have not yet succeeded in arriving at any analytic solution of the more general problem. It might be solved empirically by study of the actual distributions of spheres in a transparent supporting medium as done by W. E. Morrell.[3] I have used a semi-empirical, semi-geometrical method to find the actual values of N_n and r_n, the numbers and radii of successive co-ordination spheres in terms of N_1 and r_1.

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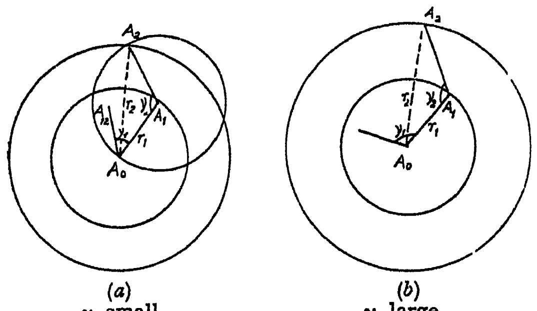
* *Note added in proof.*

It is convenient to introduce here another variable γ_1, the mean angle of closest approach of two points in the first co-ordination sphere of a third. γ_1 is clearly a function of N alone varying from about 55° in the case of 14 co-ordination ($N=14$) to 120° in 3 co-ordination ($N = 3$). If now we consider three points, A_0, A_1, A_2, each of which lies in the first co-ordination sphere of the one before it and in which A_2 forms part of the second co-ordination sphere about A_0 (see Fig. 1).



(a)
γ_1 small.
$\gamma_2 \approx 2\gamma_1$.
(A_{12} not in same plane as $A_0A_1A_3$).

(b)
γ_1 large.
$\gamma_2 \approx \gamma_1$.

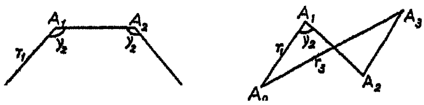
FIG. 1.

If we call the angle A_0, A_1, A_2, γ_2, the radius r_2 of the second co-ordination sphere round A_0 is given by $2r_1 \sin \frac{\gamma_2}{2}$. Now if N is large there will be another point A_{12} on the first co-ordination spheres of A_0 and A_1 and, in the latter sphere, closer to A_0 than A_2. The angle γ_2 will be approximately equal to, though always smaller than, $2\gamma_1$. Thus for irregular $N = 14$ co-ordination $\gamma_1 \approx 55°$ and $\gamma_2 \approx 100°$, while for regular $N = 12$ $\gamma_1 = 60°$, $\gamma_2 = 90°$. If N is small, however, A_2 will represent the point on the first sphere of A_1 closest to A_0 and $\gamma_2 \approx \gamma_1$. For intermediate values $2\gamma_1 > \gamma_2 > \gamma_1$.

TABLE I.

N.		γ_2°.		R_1.
14	55	100	1·6	1·9
12	60	90	1·4	1·7
10	66	80	1·3	1·5
8	74	80	1·3	1·4
6	90	90	1·4	1·7
4	109	109	1·6	1·8

Only the roughest interpolation is possible. By trial and error it is however possible to construct a table (I.) showing the relations of $N_1\,\gamma_1\,\gamma_2$ from which the values of r_2 and r_3 can be calculated. r_3 is taken to lie between $r_1(1 - 2 \cos \gamma_2)^{\frac{1}{2}}$ and $r_1(5 - 4 \cos \gamma_2)^{\frac{1}{2}}$, corresponding to possible "cis" or "trans" configuration of successive spheres (see Fig. 2), the former occurring for large the latter for small values of γ_2.



"cis" "trans"

FIG. 2.

In Fig. 3 $R_2 = r_2/r_1$ and $R_3 = r_3/r_1$ are plotted against N; the values lie on a smooth curve, making a fairly safe interpolation possible for non-integral N. The most striking feature of these curves is the way R_2 and R_3 come to a minimum for intermediate values of N (8-10).

The values of N_2, N_3, etc., as functions of N_1 are more difficult to determine. It is clear that N_2 will vary directly with N_1 and with R_2^2, but the position is complicated by the fact that, when r_1 and r_2 are close together, most of the neighbours of an A_2 point are situated in the first sphere of A_0, so that the distribution of A_2 points in the second co-ordination sphere is sparse. Some attempt to approximate to these values is shown in Fig. 4. What is important here, however, is not the possible inaccuracies of these curves, but that with sufficient study of statistical solid geometry N_2, N_3 . . . and R_2, R_3 . . . can be found as definite functions of N_1. Thus the distribution function of an ideal monatomic liquid can be written as a modification of (2) and (3).

$$g(r) = \sum_k \frac{N_k}{4\pi R_k{}^2 r_1{}^2}\sqrt{\frac{1}{\pi\lambda^2 r_1}}\, e^{-\frac{R_k}{\lambda^2}\left(\frac{r - R_k r_1}{R_k r_1}\right)^2} \quad . \quad . \quad (4)$$

In this expression, N_k and R_k are both definite, though not as yet determinable, functions of N alone. (It may be that λ is involved to a lesser degree, but as a first approximation it can be neglected.) *Any possible arrangement is therefore representable in terms of three independent variables alone*, r_1, N and λ. Clearly r_1 functions merely as a scale constant, the nature of the *configuration* depending only on N and λ corresponding to its degrees of *co-ordination* and *irregularity* respectively. These may not be entirely independent, in that certain values of N (such as 9) may only be possible if λ exceeds a certain value, while certain values of λ may not correspond to any realisable value of N, but within the permissible values N and λ may be varied independently.

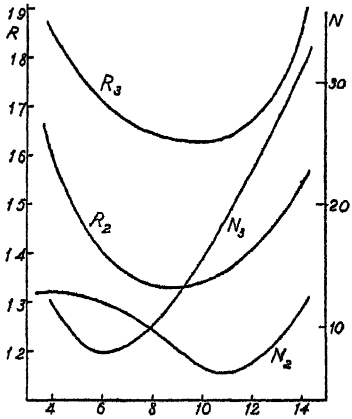


FIG. 3.

So far the argument has been purely geometrical, and would apply to any array of physical entities satisfying the conditions of homogeneous irregularity. To find what values of r_1, N and λ characterise actual monatomic liquids under different conditions, it is necessary to introduce the properties of the molecules composing them. This can be most easily done by considerations of energy. The mutual potential energy of two (symmetrically or quasi-symmetrically surrounded) molecules at a distance r_{12} apart can be expressed by the power series:

$$U_{m(T)} = \sum_q \frac{a_q}{r_{12}{}^q} \quad . \quad . \quad . \quad . \quad (5)$$

where the coefficients a_1, a_2 . . . are characteristics of the molecules only, and may be known in actual cases either empirically from crystal structures or be calculated from quantum theory. The potential energy of a liquid of any configuration whatever containing such molecules will then be

$$U_{(r_1 N\lambda)} = 4\pi\sum a_q\int_0^\infty r^{2-q} g_o(r)\,\mathrm{d}r \quad . \quad . \quad . \quad (6)$$

It is clear that in such integrations the greatest contribution will come from the nearest neighbours, and that $g_c(r)$, (3′), must be used instead of $g(r)$.

The value of U is very sensitive to r_1 and variations in λ will not effect to the first approximation the value of r_1 that gives the lowest value of U. Putting $\lambda = 0$, we have

$$U_{(r_1N)} = \sum_q a_q r_1^{-q} \sum_k N_k R_k^{-q} \quad . \quad . \quad . \quad (6')$$

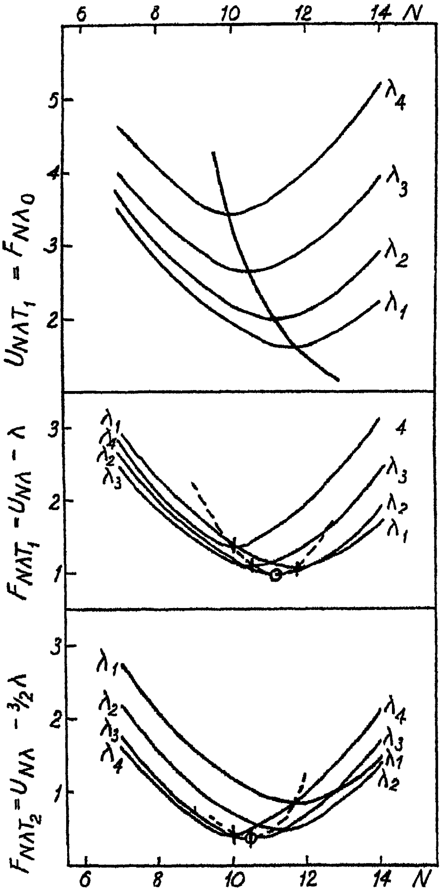
For equilibrium

$$\frac{\partial}{\partial r_1} U_{(r_1N)} = \sum_q - q a_q r^{-q-1} \sum_k N_k R_k^{-q} = 0 \quad . \quad . \quad (7)$$

This is equivalent to taking the equilibrium value of r_1 as that which gives equilibrium in the corresponding crystal. Unless λ is very large, r_1 will not vary notably from this figure.

Taking, from now on, r_1 to stand for its equilibrium value, it remains to find the equilibrium value of N and λ corresponding to any given form of (5). The expression for the energy (6) differs from that for a crystal in that the coefficients of the powers of r are not constants determined once and for all by the structure but themselves variable and in part dependent on the temperature T.

We may consider the case of a liquid to be similar to that of a solid with a number of different crystalline phases. At the transition point from one phase to another the condition that the free energy is the same for both phases must be satisfied. In the case of a liquid, the number of phases is infinite, and every temperature is a transition temperature. The condition for equilibrium is therefore that the free energy must be a minimum for all possible configurations at any temperature. To give this condition a concrete meaning, it



$U_{N\lambda}$ curves are plotted for four values of λ
$\lambda = 1, 2, 3, 4$ (arbitrary units).
$F_{N\lambda T}$ are plotted for two values of T
$T_2 = \frac{3}{2} T_1$.
It can be seen that $F_{N\lambda T_1}$ min. occurs at $N = 11{\cdot}1$, $\lambda = 2$, while $F_{N\lambda T_2}$ min. occurs at $N = 10{\cdot}5$, $\lambda = 3$.

FIG. 4.

is necessary to be able, not only to reduce the parameters defining any configuration to the smallest possible number, but to express the free energy in terms of those parameters. In this as yet I have succeeded only partially.

The expression for the free energy may be written

$$F = U - \phi T + 3kT \log \frac{h\nu}{kT} \quad . \quad . \quad . \quad (8)$$

where ϕ is the entropy due to the configuration alone.

In this form the full expression for the vibrational energy is not given. Although in any exact treatment this should be done, it will at this stage not be necessary to include it, as for all liquids except He and possibly Ne and A the thermal vibrations are fully excited and contribute $3kT \log \frac{h\nu}{kT}$ to the free energy.

The difficulty is to find an expression for ϕ. As entropy depends on the number of possible configurations of the same energy and as this depends primarily on λ we can say that ϕ is $f(\lambda)$. As the precise type of structure does not seem to be important here, we may take ϕ to be independent of N. The most plausible assumption is that $\phi = ck\lambda^2$, where c is a normalising constant. This assumption is formally sufficient to determine the equilibrium configuration, since it is only necessary to find which values of N and λ give the minimum value of F.

In its most general form (8) can now be written

$$F_{(N\lambda T)} = \frac{1}{\lambda r_1^2}\sqrt{\frac{1}{\pi r_1}}\sum_q a_q \sum \frac{N_k}{R_k^2}\int_0^\infty \Gamma_r r^{2-q}\, e^{-\frac{R_k}{\lambda^2}\left(\frac{r - R_k r_1}{R_k r_1}\right)}\, \mathrm{d}r - c\lambda^2 T + 3kT \log \frac{h\nu}{kT} \quad (8')$$

This expression can be simplified for the purpose of understanding the type of solution given, if we consider that, as a first approximation,

$$U_r = \frac{a_m}{r^m} + \frac{a_n}{r^n} \quad . \quad . \quad . \quad . \quad (5')$$

thus containing only one attractive and one repulsive term.

For equilibrium

$$r_1 = \left(-\frac{n a_n}{m a_m}\right)^{\frac{1}{n-m}} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

For different liquids m and n have different values, m varying between 2 for a metal and 6 for a rare gas and n between 10 and 20 according to the position of the atom in the periodic table.

Similarly we need only consider as a first approximation the first two terms of the distribution function. This gives for (8′)

$$F_{(N\lambda T)} = \frac{1}{\lambda r_1^2}\sqrt{\frac{1}{\pi r_1}}\int_0^\infty \Gamma_r (a_m r^{2-m} + a_n r^{2-n})\left\{N_1 e^{-\frac{1}{\lambda_2}\left(\frac{r - r_1}{r_1}\right)^2}\right.$$
$$\left. + \frac{N_2}{R_2^2} e^{-\frac{R_2}{\lambda_2}\left(\frac{r - R_2 r_1}{R_2 r_1}\right)^2}\right\}\mathrm{d}r - c\lambda^2 T + 3kT \log \frac{h\nu}{kT} \quad (8'')$$

The conditions for equilibrium are that F should be a minimum and that therefore both $\partial F/\partial N$ and $\partial F/\partial \lambda$ should vanish, using (8″) these become

$$\frac{\partial F}{\partial N} = \frac{1}{\lambda r_1^2}\sqrt{\frac{1}{\pi r_1}}\int_0^\infty \Gamma_r (a_m r^{2-m} + a_n r^{2-n})\left(e^{-\frac{1}{\lambda^2}\left(\frac{r - r_1}{r_1}\right)^2}\right)$$
$$+ \left\{\frac{\mathrm{d}}{\mathrm{d}N}\left(\frac{N_2}{R_2^2}\right) + \left\{\frac{N_2}{R_2 \lambda^2}\left(\frac{r}{R_2^2 r^2} - 1\right)\frac{\mathrm{d}R_2}{\mathrm{d}N}\right\} e^{-\frac{R_2}{\lambda_2}\left(\frac{r - R_2 r_1}{R_2 r_1}\right)^2}\right\}\mathrm{d}r = 0 \quad (10)$$

$$\frac{\partial F}{\partial \lambda} = \frac{1}{\lambda^2 r^2}\sqrt{\frac{1}{\pi r_1}}\int_0^\infty \Gamma_r (a_m r^{2-m} + a_n r^{2-n})\left\{N_1\left[\frac{2}{\lambda^2}\left(\frac{r-r_1}{r_1}\right)^2 - 1\right]e^{-\frac{1}{\lambda^2}\left(\frac{r-r_1}{r_1}\right)^2}\right.$$
$$\left. + \frac{N_2}{R_2^{\,2}}\left[\frac{2}{\lambda^2}\left(\frac{r-R_2 r_1}{R_2 r_1}\right)^2 - 1\right]e^{-\frac{R_2}{\lambda^2}\left(\frac{r-R_2 r_1}{R_2 r_1}\right)^2}\right\}dr - ck\lambda T = 0 \quad (11)$$

Although for lack of knowledge of the functions $R_2(N)$ and $N_2(N)$ these equations cannot be solved for the equilibrium values of N and λ (subsequently referred to as N_e and λ_e, yet it is possible to see from them the general nature of the solution. The best way of representing this is by means of an $FN\lambda$ diagram shown in Fig. 4.

When $\lambda = 0$ the value of N_e depends almost entirely on m. For small values of m the first two and even the third sphere contribute appreciably to the potential energy and consequently N_e is such that R_2 is small and $N_1 + N_2$ large, *i.e.* it ranges between 8 and 10. If, on the other hand, m is large, only the first sphere contributes to the potential energy and N_e is as large as possible, 12-14. As long as the potential energy function is of the simple type (5′) no lower values of N_e are possible. For such to occur either the zero point energy or directed forces must play a part.

As λ increases N_e will in general diminish, as the greater the value of N the greater the diminution due to an increase in irregularity. $U_{(N_e)}$ will increase at first more slowly, but afterwards faster than $Tc\lambda$ decreases. Where these rates are equal $\lambda = \lambda_e$ and $F_{(N\lambda T)}$ is a minimum.

Where N_e is small 4-6 an increase in λ may lead to an increase in N on account of the predominating effect of the second sphere $N_2 > N_1$; this is the case where abnormal thermal behaviour might be expected, *i.e.* negative coefficient of expansion.

It is easy to see, further, the qualitative effect of the temperature on N_e and λ_e. If T increases the entropy term increases more steeply with λ, and consequently F is a minimum with N_e smaller and λ_e larger. What functions N_e and λ_e are of T it is, however, not easy to see. The present atomic picture is, however, perfectly compatible with Prins,[4] treatment by a continuum hypothesis in which $\lambda^2 \propto KkT$, where K is the bulk compressibility. Prins' treatment does not, however, take into account changes of N with temperature and equally so with pressure; consequently the compressibility occurs in a simpler way than it does here. It is therefore unjustifiable to take over K into λ^2, but we may write,

$$\lambda^2{}_{e(T)} = kTL^2 \quad . \quad . \quad . \quad . \quad (12)$$

where L is independent of T and characteristic only of the physical type of the liquid.

Defining $N_{e(T)}$ by the relation (10) with the substitution (12), we have for the total energy (T large)

$$U_{(T)} = \frac{}{Lr_1^{\,2}}\sqrt{\frac{}{\pi r_1 kT}}\sum_q a_q \sum_k \frac{N_k}{R_k^{\,2}}\int_0^\infty \Gamma_r r^{2-q} e^{-\frac{R_k}{L^2 kT}\left(\frac{r-R_k r_1}{R_k r_1}\right)^2} dr + 3kT \quad (13)$$

where N_k, R_k are now taken to stand for functions of $N_{e(T)}$, so that U becomes a function of T only.

The specific heat at constant pressure ($p = 0$) of the liquid is given by the differential of (13).

Neglecting slowly variable terms, this is

$$C_v = \frac{1}{Lr_1^2}\sqrt{\frac{1}{\pi r_1 kT}}\sum_q a_q \sum_k \left\{\frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{N_k}{R_k^2}\right)\int_0^\infty \Gamma_r r^{2-q} e^{-\frac{R_k}{L^2kT}\left(\frac{r-R_kr_1}{R_kr_1}\right)^2}\mathrm{d}r \right.$$
$$\left. + \frac{N_k}{R_k}\frac{1}{L^2kT^2}\int_0^\infty \Gamma_r r^{2-q}\left(\frac{r-R_kr_1}{R_kr_1}\right)^2 e^{-\frac{R_k}{L^2kT}\left(\frac{r-R_kr_1}{R_kr_1}\right)^2}\mathrm{d}r\right\} + 3k \quad (14)$$

This expression falls into three parts. The first two terms of the integral are due to the change in co-ordination number (N) and irregularity (λ) respectively of the liquid configuration with the temperature. The last term here shown simply as $3k$ represents that part of the specific heat which corresponds to the degrees of vibrational freedom, and except at very low or very high temperatures will be very much the same as that of the corresponding crystal. We may, therefore, irrespective of the detailed correctness of the model chosen to represent the configuration of a liquid, write (14) as

$$C_p = C_N + C_\lambda + C_c \quad . \quad . \quad . \quad . \quad (14')$$

where C_N and C_λ stand for any expressions representing the change in energy depending on changes in equilibrium co-ordination and irregularity, and C_c stands for the value of the specific heat of the corresponding crystal.

The idea of a *configurational specific heat* for liquids, *i.e.*, of absorption of energy not in activating further degrees of freedom but in changing potential energy, is necessary to explain the observed greater specific heat of all simple (and most other) liquids compared with that of the crystals and the occurrence in certain cases, *e.g.* water, of specific heats greater than $6k$, which cannot be explained by any hypotheses depending on degrees of freedom only.

To compute such a specific heat is as yet impracticable, as the functions N_k, R_k are not well enough known, nor do the equations (10), (11) for N_e and λ_e lend themselves to easy solution. A way of testing the theory numerically would, however, be provided if we could measure $g(r)$ and consequently N_e and λ_e at different temperatures for a monatomic liquid, but this has not as yet been done experimentally.

Meanwhile it is possible to find in a qualitative way the explanation which the proposed model would give for other properties of liquids.

So far the effects of pressure on a liquid configuration have not been considered, the whole treatment being based on conditions of equilibrium at zero pressure. A similar but more complicated treatment could be made for constant volume or density; this is equivalent to introducing the condition

$$\underset{r\to 8}{\mathrm{L}}\ \frac{3}{r^3}\int_0^r r^2 g(r)\mathrm{d}r = \underset{k\to\infty}{\mathrm{L}}\ \frac{3}{4\pi R_k^3}\sum_1^k N_k = \rho = \frac{1}{v} \quad . \quad (15)$$

For any value of ρ or v it would then be necessary to find the equilibrium configuration, using (15) as a limiting condition instead of (6), which would no longer hold. The pressure would be given from (13) by

$$\frac{\mathrm{d}U_{(T)}}{\mathrm{d}v} = p \quad . \quad . \quad . \quad . \quad . \quad (16)$$

It is not difficult to see qualitatively what effects change of volume would have on the equilibrium configuration. Diminished volume would lead to greater regularity. r_1 and λ would both diminish, N increase. The effect of pressure on a liquid, unlike its effect on a crystal, is not only taken up with altering uniformly the distances between molecules. We may indeed consider the compressibility of a liquid to fall into two parts, the normal compressibility due to changes in r_1 which will be roughly the same as for a crystal and the *configurational compressibility* due to changes in N and λ. In a similar way, the thermal expansion can be seen to have a configurational term. For constant volume, increase in temperature would diminish N to a lesser degree, and increase λ to a greater degree, than for constant pressure, while r_1 would also diminish. This is in accordance with X-ray observations, which are more sensitive to N than λ and show little variation of pattern with temperature at constant volume even above the critical point. The specific heat at constant volume might be calculated directly from that at constant pressure, for both the compressibility K and the thermal expansion α appearing in the relation

$$C_p = C_v + \tfrac{1}{2}\frac{\alpha}{K}$$

can be derived in principle from (13) or (15).

It can, however, be seen directly that the term C_N in (14) will be less for constant volume and that this will more than compensate any change in C_λ. The theory as it stands, however, will not account for the fall in C_v for nearly all liquids from a value $> 3k$ to approximately $2k$ at the critical point.[5] This effect is probably to be referred to the vibrational term C_e in (14). At high temperatures the degrees of freedom are not purely vibrational but something intermediate between vibrational and translational.

Of particular interest is the possibility of examining in the light of this hypothesis the relations between the structure of liquids and crystalline solids. It might seem at first sight as if, on cooling, the configuration of any simple liquid would pass continuously through a diminution of λ into that of the corresponding crystal. That this, in general, cannot be so, can, however, be seen by comparing the expressions for the free energies of the liquid derived from (8′) by substituting L^2kT for λ and N_e for N:

$$F_{l(T)} = U_{l(T)} - T\phi$$

$$= \frac{1}{Lr_1^2}\sqrt{\frac{1}{\pi r_1 kT}}\sum_q a_q \sum \frac{N_k}{R_k^2}\int_0^\infty \Gamma_r r^{2-q}\, e^{-\frac{R_k}{L^2kT}\left(\frac{r-R_k r_1}{R_k r_1}\right)^2} dr - cL^2kT + 3kT\log\frac{h\nu}{kT} \quad (16)$$

with that of the crystal composed of the same atoms, derived from (6′)

$$F_{c(T)} = U_{c(T)} = \sum_q a_q r_1^{-q} \sum_k N_k R_k^{-q} + 3kT\log\frac{h\nu}{kT} \quad (17)$$

The first terms in each expression, though differing in complexity, are essentially of the same type, the only difference being that $U_{l(T)}$ is always greater than $U_{c(T)}$ and increases slightly with T owing to the increase of N and λ. This is more than counterbalanced at low temperatures by the entropy term $cL^2k^2T^2$ occurring only in the liquid so that $\frac{dF_l}{dT} < \frac{dF_c}{dT}$. We may think of this as due to the possibility of the liquid finding a configuration of lower free energy in a way impossible for the crystal with a fixed configuration and, consequently, having a free energy curve rising more slowly with the temperature. The curves must therefore in general cut ($F_l(T) = F_c(T)$) and cannot form a continuation of each other. An exception may occur at low temperatures where owing to the rapid change of the characteristic frequency in the liquid $\frac{dF_l}{dT} > \frac{dF_c}{dT}$.

The latent heat of fusion is given by

$$L = U_l(T_m) - U_c(T_m) ; \quad . \quad . \quad . \quad (18)$$

it will be large only if r_1 and N_k are markedly different for liquid and crystal, a condition which will only occur when N_1 is small.

The relation between liquid and crystal may be studied from another and more fundamental point of view. Without involving energy considerations, we may ask whether it is possible to construct a series of distribution functions forming a continuum between an ordered and disordered state. There are purely formal reasons for believing this is not possible for either two- or three-dimensional aggregates, though it is so for the one-dimensional case. The simplest approach is through the study of two-dimensional aggregates. I have constructed a number of such aggregates, both regular and irregular, and it is fairly easy to see that the distribution functions fall sharply into two classes. Up to now it has proved impossible to produce distribution functions for which the root mean square deviation is $> 0{\cdot}05r$ and $< 0{\cdot}2r$ approximately. The practical reason for this can be seen from Fig. 5 (page 279). Starting from a regular, close-packed hexagonal aggregate, the distance of one atom from its nearest neighbours can be varied, but unless co-ordination changes in one place from the normal co-ordination 6 to that of 7 or 5, the configuration will remain regular. If, on the other hand, one place of 5 co-ordination is introduced, it is practically impossible to return again to a regular arrangement of an area containing less than 100 points, and in that area considerable variation both of co-ordination and mean distance of nearest neighbours occurs. In another way of looking at the problem, *the existence of points of abnormal co-ordination* is the characteristic of the liquid state. In this way the theory suggested here links up with the more formal picture presented by Eyring,[6] in which the liquid state is considered as an ordered solid containing a number of holes. Such a picture cannot represent a true molecular model, but it might be taken as a fictional starting-point of irregularity, *i.e.*, a liquid might be imagined to be produced by a solid by the removal of certain atoms and the subsequent re-arrangement of the remaining atoms to fill as nearly as possible the gaps those left. This is precisely akin to the formation of the " subtraction " structures and similar superstructures in crystalline solids, *e.g.*, γ-brass is formed from a body-centred structure of 27 unit cubes from which corner and centre atoms are removed, leaving 52 atoms in the new unit cube. Such structures occur very commonly, not only in metals but in ionic compounds, and the liquid may be considered as an extreme case in which the unit cell has become infinite, as suggested by Zachariasen.[7] Of course, it may still be (as might be implied from Prins' work) that not only one but several liquid states exist in such a case, the co-ordination *continuum being separated by regions of improbable structures.* It is impossible to decide this question with our present knowledge. My own impression is that the degree of irregularity for a liquid to exist at all is sufficient to wipe out any sharp distinction between one kind of co-ordination and another. This does not mean, however, that in general the mean co-ordination taken up in a liquid will not depend on the co-ordination of the crystal. For both depend on the nature of the potential function between the molecules of which they are composed.

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[6] *J. Chem. Physics*, 1936, 4, 283.

We have here a basis for a rough classification of liquid types. For those in which the mutual potential of any molecule falls off slowly with the distance, the co-ordination number will be large and the irregularity small. This will correspond to the state of metallic liquids.* On the other hand, if the mutual potential falls off rapidly with the distance the co-ordination number will tend to be smaller and the irregularity larger. This will be the case for molecular liquids, particularly those of the rare gases. In the extreme case, where zero point energy comes into play, the co-ordination may reach the low value of 4. Here the arguments already used about sharp distinction between liquid and solid break down, because, with such low co-ordination and rapid falling-off of potential energy with distance, a number of different configurations, regular and irregular, will have similar energies and, consequently, the transition from solid to liquid might well be of a continuous nature. This may be the explanation of the transition in so-called liquid helium, where liquid helium (II) might be considered an ideal solid in which gliding is infinitely easy and for which the consequent lack of rigidity gives the impression of its being a liquid. The question can only be solved by X-ray or electron investigations.

So far we have been considering only simple liquids, but in a qualitative way the extension to more complex liquids can easily be made. Two other factors will now enter into consideration, the shape of the molecules and the presence or absence of directive forces between them or between parts of them. We have further to consider homogeneous and heterogeneous liquids. The general scheme of liquid classification arrived at in

TABLE II.—STATES OF MATTER.

		Regular.	Intermediate	Irregular.
Coherent .	Not in configurational equilibrium	Crystal below recrystallising temperature	Anisotropic glass	Glass
	In configurational equilibrium	Crystal above recrystallising temperature	Liquid crystal	Liquid
Incoherent .	Condensed	Unrealisable		Fluid
	Expanded	Unrealisable		Gas

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* A more correct treatment of metallic liquids would be to consider not the interatomic potential function but that corresponding to the distribution of electrons in every possible configuration; thus, Brillouin zones must exist in liquid as well as in solid metals and alloys and give rise to the same magnetic and electric characters, masked, of course, to a large extent by the irregularity of the structure; thus a liquid of the composition 3Zn : 2Cu corresponding to γ brass gives a maximum, but a fairly broad maximum, of the diamagneticism composition curve. But the value of this diamagnetism is only a third of that of the corresponding crystal.

TABLE III.—TYPES OF LIQUID STRUCTURE.

Type of Intermolecular Forces		Molecular Shape.	
		Spherical.	Aspherical.
Undirected . .	Falling off slowly with distance	Liquid metals	—
	Falling off rapidly with distance	Liquid rare gases CH_4, CCl_4, C_6H_{12}, etc.	Liquid paraffins, benzene, etc.
Directed . .		Water, Ammonia, Glycerol, etc.	Long chain alcohols and acids

this way is shown in Table III. The factor of molecular shape becomes important in liquids only if the variation of the shape from the spherical is very marked. Under the conditions of irregularity in the liquid the possibility of rotation of molecules and their consequent assumption of a quasi-spherical character are very much greater than in the solid, and we already know that molecules whose length is of the order of two or three times their breadth can often rotate in the solid state. With longer or flatter molecules there will be a tendency for limited parallelism. If this is confined to a hundred or less molecules, we get the cybotactic state discussed by Stewart. If the number rises into thousands, we have already one of the varieties of liquid crystal. The existence of directed forces, whether they are homopolar bonds, highly polarised ionic bonds, or the weaker hydrogen or hydroxyl bonds, tend in general to lower the effective co-ordination of the liquid, except in the special case where the bonds can form closed groups which function as quasi-molecules, *e.g.* in fatty acids or hydrofluoric acid.

The lower co-ordination produced by the existence of bonds will effect both the thermal properties and the viscosity of the liquid. Change of configuration will here be associated with greater energy and the result will be a much larger configurational specific heat and correspondingly larger viscosity. There will also be, corresponding to this, a far greater tendency to form glasses—a glass being defined as a super-cooled liquid in which the viscosity has become so high that the configuration remains fixed at a state not corresponding to the equilibrium configuration but one determined by the heat treatment and the time elapsed. The most characteristic liquid of this type is water, where, as has already been shown,[8] there is a fourfold co-ordination at low temperatures due to the formation of hydroxyl bonds. Of heterogeneous liquids the most important are the ionic liquids. It would be possible to build a theory for ionic liquids similar to that outlined above for simple atomic liquids but taking into account the opposite signs of the component ions and their different radii, in other words, the condition for an ionic liquid is that the charges should be evenly distributed so as to balance one another and should obey statistically the same rules that Pauling has shown hold for ionic crystals.

The ideas expressed in this paper are obviously of a provisional character. An enormous amount of work yet requires to be done before a quantitative account of the liquid state can be profitably attempted.

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[8] Bernal and Fowler, *J. Chem. Physics*, 1933, 1, 515.

In particular we need the development of a new branch of statistical three-dimensional geometry on the theoretical side, and a much more precise experimental study of simple liquids such as those of the rare gases. For these are the only liquids which are likely to prove immediately amenable to theoretical treatment. However, it may fairly be claimed that, qualitatively, the picture presented enables one to form a general picture of the liquid state, of its transformations and of the relations between the properties of different liquids and their molecular structure.

Summary.

Starting from the assumption that the molecular structure of a simple liquid is one which is coherent and homogeneous, it is first shown that it can always be represented statistically by a distribution function determined by three variables only: the mean distance of closest approach of molecules (r_1), the number of close neighbours of any molecule (N), and the irregularity of the distribution (λ). It is next shown that the actual configuration of a particular liquid can be derived from a knowledge of the intermolecular potential function alone, by using the two conditions of minimum potential energy in relation to changes in r_1 and minimum free energy in relation to changes in N and λ. The effect of changes of temperature and pressure is shown to consist in changes in the equilibrium values of r_1, N and λ. Thus, a liquid differs fundamentally from a solid in that its configuration is not even approximately constant, but is a function of the temperature and pressure. This explains the greater specific heats and compressibilities of liquids as due to extra, configurational, specific heats and compressibilities.

It is further shown why, in general, liquids and solids cannot be considered to form part of any continuous state, as they are separated in this theory by a region of geometrically unrealisable intermediate states, and consequently why there is no reason to expect critical point phenomena between liquids and solids.

Finally, a general classification of simple and complex liquids is proposed, based on these ideas of liquid structure.

*GENERAL DISCUSSION.**

Professor H. Hellmann (*Moscow*) (*communicated*): The London dispersion forces play a great role in every theory of the liquid state. From the exposition in London's report one receives the impression that at the present time there exists no really reliable formula for the calculation of the dispersion forces between complicated molecules. In a work of mine,[8] the calculation of the dispersion forces for complicated molecules is reduced to a formula just as exact and almost as simple as that for atoms.

As is well known, for atoms we can write:

$$\epsilon = -\frac{3}{2}\frac{\alpha_1\alpha_2}{R^6}\frac{1}{1/J_1 + 1/J_2}, \quad . \quad . \quad . \quad (1)$$

where J_1 and J_2 denote a characteristic energy which, according to London, is to be identified with the ionisation energy or with the fundamental frequency in the dispersion formula of the atom. A formula first derived by Slater and Kirkwood [9] and later by Kirkwood [10] is obtained if one substitutes for J:

$$J = 240\sqrt{\frac{N}{10^{24}\alpha}}\ k\ \mathrm{cal})/\mathrm{mol}, . \quad . \quad . \quad . \quad (2)$$

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* On two preceding papers.

[9] *Acta Physicochim. U.R.S.S.*, 1935, **2**, 273.

[8] *Physic. Rev.*, 1931, **37**, 682.

[10] *Physic. Z.*, 1932, **33**, 57.

where N denotes a number of electrons. The great uncertainty in this formula lies in this number N which Slater and Kirkwood[9] placed equal to the number of electrons in the outer shell; later, however, Kirkwood,[10] upon the basis of a seemingly consistent derivation from the variation principle, set it equal to the total number of electrons in the atom. By an improved variational procedure, according to which each shell, containing approximately equally strongly bound electrons, receives its own characteristic variation parameter, I showed that instead of (1) one could write:

$$-\frac{3}{2}\sum_{i,k}\frac{\alpha_i\alpha_k}{R_{ik}{}^6}\,\frac{1}{1/J_i+1/J_k}. \quad . \quad . \quad . \qquad (3)$$

Here i applies over all the shells of one atom or molecule and k over those of the other. The quantities J are determined by (2), where now N is quite unequivocally placed equal to the number of electrons in the shells concerned. α_i and α_k signify the contribution to the polarisibility of the complete structure of the shells in question. Those of the outer shells coincide almost completely with the polarisability of the entire atom. The distribution of the polarisability can, if necessary, be estimated with sufficient accuracy. In the case of complicated molecules satisfactory data exist for distributing the total polarisibility among the individual linkages (shells of the two centre problem).

Müller's estimation, cited by Professor London, is open to criticism. One can, for instance, also derive J from the variation principle:[8]

(4)

On the other hand, for the susceptibility we have the formula:

$$\chi = N_1\frac{e^2}{2mc^2}\Sigma\overline{z_i{}^2}. \quad . \quad . \quad . \quad . \qquad (5)$$

From (4) and (5) Müller's formula follows if one identifies $\overline{(\Sigma z_i)^2}$ with $\Sigma\overline{z_i{}^2}$ and expresses them by χ given in (5). This identification is, however, not permissible, since the Pauli principle, *i.e.*, the use of antisymmetrical wave functions in the formation of the quantum mechanical mean values, leads to the result that $\overline{(\Sigma z_i)^2}$ is always essentially smaller than $\Sigma\overline{z_i{}^2}$ and consequently J, and finally the energy, are too large, as Professor London himself states. Also, according to equation (2) one obtains usually a somewhat greater value than according to London. Now I think that the J-value obtained from the consistent variation method is more reliable than the original estimation of London. (2) is valid without further ado for negative ions.

In my opinion the true problem of the dispersion forces lies not at all in a particularly exact determination of the asymptotic law for large distances, since one always employs it at distances where the theoretical assumptions of the complete derivation are not all satisfied. The rule given by Professor London (16 and 16′) is only the condition for the convergence of the perturbation calculation of the second order. It is, however, by no means the condition for the applicability of the approximated form of the perturbation potential, as well as for the neglect of other perturbation terms of second order, which at small distances are of equal importance with the dispersion terms. The consideration of higher poles has only doubtful value, since the failure of the asymptotic law at short distances has yet other causes. In an unpublished work which I carried out in collaboration with K. W. Majewski, we found that for the example of two hydrogen atoms an additivity between exchange and dispersion forces is present only down to about 3·5 Å. At smaller distances the exchange effect of the second order already plays an essential role. At distances less than 3 Å. the series development of the perturbation energy in terms of

$1/R$ is no longer permissible in a great part of the region of integration. This "Penetration effect" of the dispersion forces results in their considerable diminution, while the above-mentioned exchange terms of second order strengthen them anew. At very small distances this "Penetration effect" will be compensated chiefly through classical polarisation in the exponential fields of the atoms. However the asymptotical $1/R^6$ law renders down surprisingly well to 1·5 Å, the total energy lowering through a rigorous perturbation calculation of the second order, and indeed for the $^1\Sigma$ as well as for the $^3\Sigma$ state of hydrogen. The behaviour of rare gas like structures would in the mean lie between both cases, and one can therefore regard our results with hydrogen as supporting the usual way of calculation. One must, however, bear in mind that in extrapolation of the asymptotic law to small distances, there are included also interactions quite different from the dispersion forces, and probably in part the action of higher multipoles. If the short distance forces are taken from experiment and not, as in our example of hydrogen, from a perturbation calculation of the first order, then naturally a further compensation of error takes place.

Professor K. L. Wolf (*Wurzburg*) (*communicated*) : It was by no means van der Waals who first taught that molecules are centres of force ; it is liable to be forgotten that the kinetic interpretation of Avogadros' hypothesis implies a contraction, which has only the effect of a heuristic principle in the representation of a completely "saturated" molecule. Since chemists invariably urged that complete saturation is merely an abstract idea, the deviation of real gases from the behaviour of the ideal gas, in the molecular kinetic sense, was known before van der Waals. It is for many reasons remarkable that molecular conceptions based upon Avogadro's hypothesis should for so long and to such an extent have been visualised as real.

Dr. M. Magat (*Paris*) said: It is perhaps possible to overcome the difficulty which arises, when the London theory is applied to polyatomic molecules. Often, for smaller molecules (not more than 6-7 atoms) we can introduce, instead of local polarisibility, the anisotropic tensor of polarisability, *i.e.*, a slightly different polarisibility in each direction. This tensor is known from the Kerr effect and the polarisation of the diffused light. In other terms we may consider, instead of the real model, a Langevin molecule. This correction is particularly important in cases where there is no free rotation.

Mr. J. D. Bernal (*Cambridge*) said : I am particularly interested in the case of liquid helium. I think it must provide an exception, but an understandable one, to the general theory of liquids put forward in my paper. Here, as Professor London has pointed out, the kinetic energy of the atoms is great compared with potential energy, leading to a low co-ordination number, but also perhaps giving the possibility of a continuous transition from the liquid to the crystalline state. This is what I imagined to occur at the so-called λ point. In my view liquid helium II is really a crystalline solid with a diamond structure, but owing to the wide amplitude of vibration it will possess no rigidity and will be, from the physical point of view, a perfect fluid. This is in accordance with the remarkable low viscosity and high thermal conductivity of the substance. It should be noted that a similar rapid decrease of viscosity on cooling is observed in the formation of liquid crystals from very isotropic liquids. But the state of liquid helium II will differ from that of liquid crystals (in the fact that here a three-dimensional and not merely a two-dimensional order is achieved, and, secondly, that none of the orientation or optic phenomena usually associated with liquid crystals should be observed. The only way of testing this hypothesis would be by means of X-rays or electron diffraction.

Professor F. Simon (*Oxford*) said : It would, of course, be interesting to compare Mr. Bernal's theory with experiment, and it seems to me that the best point for comparison would be the part of the specific heat which

Mr. Bernal calls the configurational specific heat. The notion of these specific heats was introduced by me some years ago.[11] I also derived experimental values for this part of the specific heats for glycerol and found them very high. These data can now be given for many more liquids, although of a more complicated structure than the case treated by Mr. Bernal. I hope it will be possible for Mr. Bernal to extend his theory to cover these cases, so that the experimental material available may be used for testing it.

As to the case of liquid helium, I think it is certain that it will be in an ordered state at very low temperatures, as I have often pointed out in the past. Whether one calls this ordered state a crystal or not is largely a question of nomenclature. I would prefer [12] still to call it a liquid, even if it passes gradually into an ordered state, and to call this state one of "liquid degeneracy." I shall discuss this question elsewhere in detail, but I mention it here only that one of my chief reasons for this view is that there is no phase change in the normal sense between the two forms of liquid helium and that besides the "ordered" liquid helium there still exists the normal solid as a separate phase.

Professor E. Bauer (*Paris*) said : Mr. Bernal's very interesting theory is a purely geometrical one. My paper [13] shows that any possible equation of state for liquids must involve essentially the data at the melting-point. Therefore a theory of liquids can only be satisfactory if it is dynamical and explains fusion.

From Mr. Bernal's point of view, melting can be described as follows : the principal characteristic of a crystal is perhaps a strict connection at a distance between the elements of the lattice. The average orientation of two molecules, even far apart, is parallel, and their average distance is constant (diffusion being neglected). A very simple but important remark of Peierls shows that this connection is only possible in a polydimensional lattice where "messages" between distant molecules can be transmitted through circuitous ways, when the direct one is perturbed by thermal fluctuations.

In a liquid those messages get lost, the connection at a distance no longer exists, whereas the local organisation partially remains : for this reason the transverse waves are no longer propagated through macroscopical distances.

The process of fusion seems essentially due to two causes :

(1) *Dilatation.*—Melting can begin when the average molecular distance is such that the elastic force begins to diminish when the amplitude of molecular vibration grows (inflexion point of the potential curve) (Raschewsky).

(2) *Thermal Fluctuations.*—The average potential curve of a molecule in the solid body is not identical with the mutual potential curve for two isolated molecules. It is a function of the Madelung number and of the thermal fluctuations. The average curve has yet another shape in the liquid. At the melting-point the potentials are such that the free energies are equal in both phases ; at higher temperature the lattice gets instable.

The theory of Herzfeld and Göppert-Mayer, though taking fluctuations into account, is related to Raschewsky's point of view and seems not to touch the essential part of the problem. The theory of Bartholomé and Eucken describes the liquid in a rather too statical way.

Professor J. A. Prins (*Wageningen*) said : Most of the calculations indicated in Bernal's paper cannot be performed explicitly in the three-dimensional case. Workers wishing to get acquainted with their meaning may find it instructive to solve the analogous problems in one dimension where only elementary analysis is required.

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[11] *Ergebn. exakt. Naturwiss.*, 1930, 9, 248, discussed in detail in a second paper. *Z. anorg. Chem.*, 1931, **203**, 219.

[12] See my contribution, p. 65.

[13] *This vol.*, page 81.

I agree with Professor Bauer's suggestion that the one-dimensional model is not capable of representing the phenomenon of melting. I think, however, that the inadequacy of the one-dimensional model for the process of melting is due to a failure of the one-dimensional model to represent the solid state rather than the liquid state.

Professor J. H. Hildebrand (*Berkeley, Cal.*) said : Is it not very desirable that experimental checks upon this important theoretical work be furnished by determinations of liquid structure over a wide range of temperature, particularly into regions where the liquid is greatly expanded over the closest packed structure ?

The investigation of the structure of a model liquid, to which reference has been made in this discussion, was carried out by one of my students, Mr. W. E. Morrell. A number of uniform gelatin spheres were made by freezing drops of solution in a column of cold oil. A small proportion of these were coloured. A mass of these spheres was immersed in a cubical vessel in a gelatin solution which had been boiled to prevent gelation, but which had the same density and refractive index as the spheres, which, except for the coloured ones, were therefore invisible. The cell was agitated and spark photographs taken, from which the three dimensional co-ordinates of the coloured spheres could be measured. A large number of such measurements permitted the calculation of the frequency of radial distribution, which was found to agree with the pattern found by X-rays for mercury.

Professor F. London (*Paris*), said, in reply : I am not convinced that Professor Hellmann's equation (3) represents a "really reliable" formula for the calculation of dispersion forces between polyatomic molecules.

(1) It is well known that there is no indication to believe that one can uniquely distribute the proper frequencies of an atom among its different shells of electrons. One cannot identify the numbers 2, 8, 18, etc., of electrons in the single shells with a corresponding subdivision of the sum of the oscillator strengths. Especially for the rare gases it seems impossible to say which frequencies belong to the outer shell.

(2) Nor can I agree that the variation method of Slater and Kirkwood is a particularly "reliable" method. The variation method necessarily uses very simplified expressions for the *eigen*functions of the unperturbed atoms (products of one-electronic *eigen*functions) and starts, accordingly, from a very inexact value of the internal energy of the isolated atoms. It seems very difficult to estimate which error is due to the fact that only that very small part of the total energy which is formed by the interaction energy, and not the total energy, is concerned.

(3) Our simplified expression (13), moreover, obviously does not claim to be particularly exact. But the relation of formula (15) to the dispersion formula is an *exact* law, and this allows the estimation of the possible error of (13) and its improvement by additions of further terms, in any single case, according to the progress of our empirical knowledge of the dispersion curve. The remark of Mayer on the decisive contribution of the continuous ultraviolet absorption in the case of the rare-gas-like ions is a particularly interesting example of the utility of our knowledge of the optical properties of molecules for the determination of their molecular forces. For these rare gas-like ions in particular, the Slater-Kirkwood formula gives far too small attractive forces (up to 50 per cent. too small) ; they would not account, *e.g.*, for the transition from the NaCl type to the CsCl type.

Finally, I wish to emphasise, that the rule (16) (16′) is by no means a criterion for the convergence of the second order of the perturbation calculus. Its meaning is rather the following : If condition (16) is fulfilled, this indicates that we have an interaction only in the second (or higher) order of the perturbation calculus ; this is the interaction chiefly discussed in my report. If, however (16) is *not* fulfilled, this indicates that *even in the first order* a peculiar interaction appears, which must first be considered. The convergence of the developments is in no way touched by condition (16).

Mr. J. D. Bernal (*Cambridge*), in reply, said: It is naturally more difficult to expand the theory to liquids with complex molecules, in particular those containing hydroxyl bonds. In this case it would be necessary not only to have a distribution function for centres of the molecule but also mutual distribution functions of a higher order of complexity than the relative orientation of neighbouring molecules. Of course it will turn out, in a great number of cases, that the stable state is one in which free rotation of the molecules occurs and for this the simplified theory will still hold. In the particular case however of hydroxyl or hydrogen bonds the relative position of two neighbouring molecules will in general be more important than the distance apart of their centres. In this case a simplified theory might be tried, as indicated in my original paper on water, namely, that the energy of the liquid should be counted as the sum of the energies of the hydroxyl bonds. At high temperatures the probability that every molecule will have its full quota of such bonds will be diminished. The potential energy will consequently rise and there will be an extra large term in the configurational specific heat as pointed out by Professor Simon.

I have chosen to deal with the two and three dimensional cases precisely because here alone there is a sharp geometric distinction between crystal and liquid. My theory does give a formal account of the transition between these two states involving a discontinuous jump over unrealisable configurations. It is not so far removed from the dynamical theory which Professor Bauer wants, as the free energy is taken into account throughout. I realise, however, that there is a long way to go before the theory is put on a proper quantitative basis.

I do not attach any great importance to the particular formulæ contained in my paper. Its value, it seemed to me, lies in suggesting that the state of a liquid under any conditions can be referred to a small number of variables: That the free energy should be expressible in terms of those variables, that the condition of its being a minimum fixed relations between them and finally that on heating a liquid the increase in potential energy due to its greater looseness of texture will be balanced by the increase of general irregularity and consequently of entropy of the molecular positions.

In reply to Professor Frenkel's criticisms I should like to point out that my N is not the integral value of the number of neighbours around any individual molecule but the—in general non-integral—statistical mean of all neighbours in the liquid which is consequently liable to continuous variation. Further, far from neglecting the vibrations about quasi fixed equilibrium positions of the atoms in a liquid, these are assumed to be the same as in a solid as will be seen in the paragraph at the head of page 33.

THE DEPENDENCE ON TEMPERATURE OF THE SPECIFIC HEAT (C_v) OF MONATOMIC LIQUIDS.

By E. Bartholomé and A. Eucken.

Received in German, 5th August, 1936, and translated by W. J. C. Orr.

1. Older Attempts to Calculate the Influence of Temperature on the Specific Heats of Monatomic Liquids.

The determination of specific heats has for long provided important material for investigating the types of atomic or molecular motion in different states of aggregation. For example, the vibrational and rotational heats of gases are now quantitatively reproduced by quantum theory functions and thus one can conclude that the models of the harmonic oscillator or rotator deduced from theory (taking account of nuclear spin) portray the molecular motion satisfactorily. Likewise, the temperature variation of the atomic heats of solids shows that the fundamental assumption, in Debye's theory, of coupled harmonic vibrations of the lattice elements correctly describes the thermal motion of a simple monatomic solid.*

It was natural therefore to seek information about the molecular motion of liquids also, from studies of their specific heats. We shall here consider only liquids composed of monatomic atoms, whose thermal motion can only consist in a three-dimensional movement of the centre of gravity (*Schwerpunktbewegung*). This movement contributes to the specific heat for gases $3/2R$, while for solids it degenerates into harmonic vibrations round a definite equilibrium, and according to Debye may contribute up to $6/2R$.

For the liquid state, an intermediate value between these limits is to be expected and it is illuminating that at low temperatures liquids approximate to the solid state,† while at high temperatures they tend steadily towards the gaseous state.

The available experimental data are in agreement with the above general ideas. For He,[1] C_v rises from 1·42 at 2·4° to 1·82 at 4·3°; at 20°, *i.e.* above the critical point, but where the density of the liquid is near that at its boiling-point, it is still rising slowly at about 3 cals.[2] Below 50°, H_2 has no rotational heat, and is therefore classed thermally as a monatomic molecule. Between 15° and 35° [2, 3] it shows slow rise in C_v from 2·4 to 3·5, while for D_2 between 18° and 23°, C_v is constant at 3·5. For the rare gases Ne [4] and A,[5] C_v decreases slowly with rising temperature from about 6 cals. at the melting-point. Similarly, in the case of the monatomic metals Hg [6] and Na.[7] † C_v decreases with rising temperature; although the limiting value at $T = \infty$ cannot be decided with certainty, there seems no reason to doubt it is 3 cals.

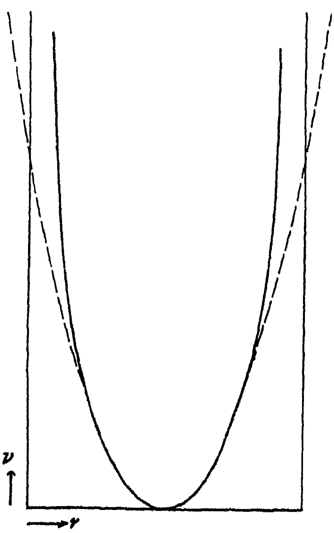

FIG. 1.

Eucken [8] has shown that there ought to be an approximate universal function reproducing the whole temperature variation, a small part of which would represent the observations on any particular substance over only a small temperature interval. Eucken and Seekamp[9] have given precision to the physical conceptions which could explain the observed temperature variation of this function. At low temperatures the atoms vibrate just as those in the solid state; the amplitudes are so large, however, that the ideal case of the harmonic oscillator can no longer be employed. While in the case of the harmonic model the amplitude continues to increase with increasing energy, in the case of liquids there is speedily obtained a maximum elongation, determined by the distance between the two molecules (Fig. 1), so that a rise in temperature will then not materially alter the amplitude. The thermal motion approximates more and more to a zig-zag movement, which must tend to the limiting value $C_v = 3$ at higher temperatures.

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* At low temperatures, of course, Debye's approximation to the atomic structure leads to characteristic deviations. *Cf.* N. Blackmann, *Proc. Roy. Soc. A*, 1935, 148, 405.

† This similarity between solid and liquid phases is claimed by Frenkel (Acta, *physicochem.* 1935, **3**, 633), as a new aspect in treating liquids; it has, however, been current since the time of Boltzmann, and has since been employed by a whole series of investigators, *cf.* refs. given by Eucken.[8]

[1] W. H. Keesom and A. P. Keesom, *Comm. Leiden* 235d (1935).

[2] A. Eucken, *Ber. Ak. Wiss. Berlin*, 1914, **22**, 682.

[3] E. Bartholomé and A. Eucken, *Z. Electrochem.*, 1936, **42**, 547.

[4] K. Clusius, *Z. physik. Chem.*, *B*, 1929, **4**, 1.

[5] A. Eucken and F. Hauck, *ibid.*, 1928, **134**, 161.

[6] A. Magnus, *Z. anorg. Chem.*, 1928, **171**, 73.

[7] A. L. Dixon and W. H. Rodebush, *J. Am. Chem. Soc.*, 1927, **49**, 1162.

[7] † These authors deal with C_p, which they find decreases with rising temperature. Since the difference $C_p - C_v$ increases with temperature in all previously investigated cases C_v would thus have a negative temperature coefficient.

[8] A. Eucken, *Verhdl. deutsch. phys. Ges.*, 1916, **18**, 18.

These ideas have been used by most authors who have attempted to calculate the specific heat of liquids. They form also the physical basis for the considerations of this paper. The various authors differ in the way in which these ideas are formulated quantitatively. Eucken [2] treated the first deviations from harmonic behaviour by introducing in the Debye function a limiting frequency, which increased with rising temperature, *e.g.* in Fig. 1 he introduced into the invariant walls of the potential box parabolas of curvature increasing as the temperature increased. Using an empirical law $\nu \sim \sqrt{E}$ he obtained complete agreement with his results for H_2. However, his law led to the limiting value 6 cals., and did not give the decrease associated with Ne and A. With $\nu = aT^n$ $(n > 1)$, Magnus obtained a decrease of C_v from 6. A still larger temperature dependence in the form, $\ln\nu/\nu_0 = A + qT^n$ was introduced by Damköhler,[10] who, of course, was considering only solid bodies; this implies that the vibrations are harmonic up to very near the maximum amplitude, but that, with a further increase of energy, the frequency which determines the steepness of the parabolas increases exponentially. Eucken and Seekamp,[9] then gave up the attempt to approximate the potential curves by parabolæ and introduced instead a repulsive force occurring during collision of the form a/r^n. Since the discrete energy levels of this potential cannot be given, the calculations were limited to the classical region, wherein they obtained a slow decrease of C_v. The calculations were, however, necessarily made numerically at a very early stage and, owing to the work involved, were restricted to the case of argon. Generalisation from the final results is therefore not possible.

Brillouin,[11] on the other hand, assumes that liquids behave exactly like solids as far as longitudinal vibrations are concerned, and arrives, for this motion, at a Debye function. For liquids not having transverse vibrations, he introduces free rotation and obtains a limiting value of 4 cals. for high temperatures, while at low temperatures his C_v curve decreases regularly. We consider the physical basis of this theory highly problematical, so that the conclusions drawn from the quantitative and qualitative deviations from theory of the experimental C_v curves, *viz.*, the occurrence of crystalline regions in liquids far above the melting-points (indeed, right up to the critical point !), appear to us lacking in cogency.

2. The Teller-Pöschl Potential.

To derive a universal function for C_v a new point of attack seems desirable. Now, one part of the function can probably be constructed by calculations which approximate to the limiting case of solids, but our model must be applicable without extrapolation to liquids.

[9] A. Eucken and H. Seekamp, *Z. physik. Chem.*, 1928, 134, 178.
[10] G. Damköhler, *Ann. Physik*, 1935, *V*, 24, 1.
[11] L. Brillouin, *J. Physique Rad.*, 1936, 7, 153.

For our purpose, the potential, which Teller and Poschl [12] investigated in another connection, appears suitable and has the form:

$$V = \frac{h^2}{32md_0^2}\left[\frac{a(a-1)}{\sin^2\frac{\pi}{2d_0}(r-r_0)} + \frac{a(a-1)}{\cos^2\frac{\pi}{2d_0}(r-r_0)}\right] \quad . \quad (1)$$

where h is Planck's constant, m the mass of the oscillator, d_0 the width of the potential box and a a parameter > 1, but not necessarily an integer. The potential curve for $a = 2$ is shown in Fig. 2.

When $\frac{\pi}{2d_0}(r - r_0) = 0$ or $= \frac{\pi}{2}$, V is infinite, but when it equals $\frac{\pi}{4}$ there is a minimum, corresponding to the equilibrium position of the molecule. The smaller a is, the flatter is this minimum. For $a \rightarrow 1$ it becomes the simple box potential (*i.e.*, pure translation with reflexion at two fixed walls), already treated by de Broglie. At small energy contents the molecule vibrates harmonically round the equilibrium position, the frequency being,

$$\frac{1}{2\pi}\sqrt{k/m} = \frac{1}{2\pi}\sqrt{\frac{d^2V}{dr^2}\Big/m} = \frac{h}{16md_0^2}\sqrt{a(a-1)} \quad . \quad . \quad (2)$$

From (2) the physical interpretation of the parameter a is clearly the measure of the restoring force for small displacements. With increasing energy content, if the potential curve is spread out wider, the restoring force increases at a greater rate than the elongation and tends asymptotically to ∞ when the elongation is equal to the width of the box.

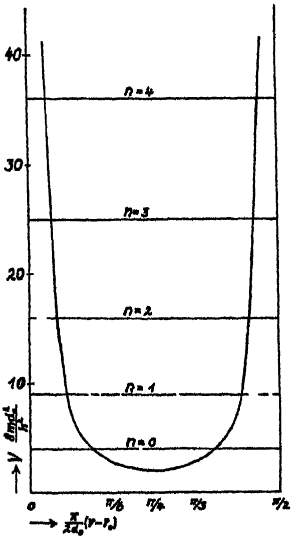

FIG. 2.

These facts alone can qualitatively describe the C_v curve. At low temperatures the function will increase like a Planck-Einstein function. The smaller the parameter a, the sooner deviations from this function occur, so that C_v becomes smaller than the Planck-Einstein value. At high temperatures the curve tends asymptotically to 3 cals. In the intermediate region a maximum of unknown height must occur, since the box potential also exhibits a small maximum.

This potential not only fulfils all the conditions necessary to reproduce the behaviour of liquids, but also has the great advantage, as Teller and Pöschl showed, that in this form the Schrödinger equation may be readily integrated. Its Eigenvalues are of the simple form:

$$E_n = \frac{h^2}{8md_0^2}(a+n)^2 = B(a+n)^2 \quad . \quad . \quad . \quad (3)$$

where B is written for $\frac{h^2}{8md_0^2}$, n is a positive integer and can be regarded as a quantum number. From the energy values, also, one can easily see the continuous transitions from harmonic vibrations to translation. For large values of a, the first energy levels are approximately equidistant, as in the case of the oscillator, whereas when $n \rightarrow \infty$ the spacing of the energy levels varies quadratically as in the case of the box potential.

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[12] G. Pöschl and E. Teller, *Z. Physik*, 1933, 83, 143.

Knowing these energy values, the calculation of C_v throughout the whole temperature range offers no further difficulty; if they are introduced into the "state sums" (Zustandsummen) C_v is given by the familiar expression :

$$\frac{C_v}{R} = \frac{\sum\limits_{n=0}^{\infty}\left[\frac{B}{kT}(a+n)^2\right]^2 e^{-\frac{B}{kT}(a+n)^2}}{\sum\limits_{n=0}^{\infty} e^{-\frac{B}{kT}(a+n)^2}} - \left[\frac{\sum\limits_{n=0}^{\infty}\frac{B}{kT}(a+n)^2 e^{-\frac{B}{kT}(a+n)^2}}{\sum\limits_{n=0}^{\infty} e^{-\frac{B}{kT}(a+n)^2}}\right]^2 . \quad (4)$$

Table I. shows the values of C_v/R calculated for a series of B/kT values and for values of the parameter a from 1 to 10; for $B/kT \geqslant 0{\cdot}1$

TABLE I.

B/KT a	2.	1.	0·8.	0·6.	0·4.	0·2.	0·1.	0·01.	0·005.	0·003.
1	0·089	0·426	0·493	0·543	0·562	0·556	0·542	0·514	0·510	0·508
2	0·046	0·172	0·289	0·517	0·579	0·636	0·619	0·542	0·530	0·523
3		0·044	0·138	0·263	0·486	0·665	0·676	0·569	0·549	0·539
4			0·084	0·138	0·357	0·648	0·715	0·596	0·569	0·554
5				0·119	0·239	0·604	0·738	0·622	0·587	0·569
6				0·033	0·152	0·546	0·754	0·644	0·606	0·583
7					0·083	0·472	0·730	0·667	0·623	0·598
8					0·056	0·400	0·711	0·688	0·640	0·611
9						0·331	0·687	0·708	0·657	0·625
10						0·271	0·654	0·726	0·672	0·639

the calculation was done by direct summation; for the smaller values it is more convenient to use an integration method. The summations occurring in (4) may be represented in this case with sufficient accuracy by the following expressions : *

* For $\sum\limits_{n=0}^{\infty} e^{-\frac{B}{kT}(a+n)^2}$, the proof may briefly be written as follows:

$$\sum_{-\infty}^{+\infty} e^{-\frac{B}{kT}(a+n)^2} = \sum_{-\infty}^{+\infty} e^{-\frac{B}{kT}m^2} = \sum_{-\infty}^{+\infty} e^{i\pi\tau m^2}\left(\tau = \frac{iB}{\pi kT}\right) = \sqrt{\frac{i}{\tau}}\sum_{-\infty}^{+\infty} e^{-\frac{i\pi}{\tau}m^2}$$

$$= \sqrt{\frac{\pi kT}{B}}\sum_{-\infty}^{+\infty} e^{-\frac{\pi^2 m^2 kT}{B}} = \sqrt{\frac{\pi kT}{B}}\left(\text{for } \frac{B}{kT} > 0{\cdot}1\right).$$

Moreover

$$\sum_{m=1}^{\infty} e^{-\frac{B}{kT}m^2} = \frac{1}{2}\sqrt{\frac{\pi kT}{B}} - \frac{1}{2}.$$

and $$\sum_{n=0}^{\infty} e^{-\frac{B}{kT}(a+n)^2} = \frac{1}{2}\sqrt{\frac{\pi kT}{B}} - \frac{1}{2} - e^{-\frac{B}{kT}} \dots - e^{-(a-1)^2\frac{B}{kT}}.$$

$$\sum_{n=0}^{\infty} e^{-\frac{B}{kT}(a+n)^2} = \frac{1}{2}\sqrt{\frac{\pi kT}{B}} - \frac{1}{2} - e^{-\frac{B}{kT}} \dots - e^{-(a-1)^2\frac{B}{kT}}$$

$$\sum_{n=0}^{\infty} \frac{B}{kT}(a+n)^2 e^{-\frac{B}{kT}(a+n)^2} = \frac{B}{kT}\left[\frac{1}{4}\left(\frac{B}{kT}\right)^{-\frac{1}{2}}\sqrt{\pi} - e^{-\frac{B}{kT}} \dots \right.$$
$$\left. - (a-1)^2 e^{-(a-1)^2\frac{B}{kT}}\right] \qquad (5)$$

$$\sum_{n=0}^{\infty} \left[\frac{B}{kT}(a+n)^2\right]^2 e^{-\frac{B}{kT}(a+n)^2} = \left(\frac{B}{kT}\right)^2\left[\frac{3}{8}\left(\frac{B}{kT}\right)^{-\frac{1}{2}}\sqrt{\pi} - e^{-\frac{B}{kT}} \dots \right.$$
$$\left. - (a-1)^4 e^{-(a-1)^2\frac{B}{kT}}\right].$$

For $B/kT < 0{\cdot}1$ the summations in (4) are calculated by formulæ (5). The table satisfies our earlier qualitative conclusions upon the asymptotic behaviour at high and low temperatures. We see also that the C_v curves rise at higher temperatures and reach a higher maximum the greater a is; at large a's, the harmonic approximation holds up to high temperatures, but for $a = 1$ (pure translation), the C_v curve rises, as was emphasised before, from 0 to values $> R/2$ and, with rising temperature, reaches the above limiting value. All curves are characterised by a rise of the specific heat to a maximum and, in still greater measure, in that the subsequent decrease is completed very slowly. One has also to expect, as is actually the case with liquids, a dependence of C_v on temperature through a very wide region.

It may be thought troublesome that this potential contains two independent parameters, as to which nothing can be asserted *a priori*, while in the model of the harmonic oscillator only one parameter ν is involved. There are, however, actually two parameters in the case of the harmonic oscillator, *viz.*, the mass m, and the restoring force, k. By (2), k can be expressed in terms of the parameter a, so that the two quantities are equivalent. For our more general potential, the only peculiarity of the harmonic laws that is lost is that the quantities k and m always occur combined as a ratio k/m, which may therefore be expressed as a constant frequency ν. The Teller-Poschl potential thus offers a quite natural generalisation of the harmonic potential.

3. Comparison of the Theoretical C_v Curves with the Experimental Data.

The application of these results to real liquids is, in a physical sense, a little arbitrary. The transition from equidistant to quadratically spaced energy levels could also be obtained from similarly constructed potentials. Thus one could visualise a potential which becomes infinite not just on the walls of the box, but at a distance r, which can be considered as the radius of the impenetrable molecule; for such a potential, however, the Schrödinger equation cannot be integrated in finite terms. The introduction of such a potential cannot, however, change the course of the curve qualitatively, although smaller quantitative deviations, especially at low temperatures, remain to be taken into account.

Although the potential under consideration was derived for the one dimensional case, the generalisation to 3 translatory degrees of freedom presents no difficulty, for, if it is supposed that the three translations are mutually independent, multiplication of the figures in Table I. by 3 will give the three dimensional case.

Another difficulty is more important. The quantity d_0 represents twice the maximum elongation of the vibrating mass point. This will depend on the macroscopic density, from which the mean distance between the centres of gravity of the molecules can be directly calculated. The solid rare gases and solid H_2 possess the closest spherical packing ; the volume change on melting is so slight that one can assume the closest spherical packing with good approximation for the liquids also. With this assumption the mean molecular distance d is given by the formula :

$$N\frac{\pi}{6}d^3 = 0{\cdot}7V.$$

This value of d could be substituted for d_0 in (1) if the molecules were completely penetrable. This assumption is, however, untenable, so that one must now subtract from the distance d the minimum distance d^1 to which the centres of gravity can approach ; d^1 cannot be determined exactly, but may be approximated with sufficient accuracy.*

However, with given macroscopic densities, the maximum elongation will not be the same for all molecules. For a " most probable " box width, which we could put with fair certainty as the mean maximum elongation, there will be a greater and a smaller maximum elongation. The partition function of this elongation will fall more rapidly on both sides of the most frequent values, the greater the *Eigenvolume* of the molecule is, in proportion to the total volume. In the region of normal liquid densities, box-widths of about twice the molecular distances will be very improbable. So long as nothing more precise is known about the partition function, a very fair approximation is given by using constant d_0.

So far we have treated the case of the free oscillator only. To transpose our results to real liquids, we must remember that the oscillators are not free but will, as in solids, be coupled with their neighbours. The direct application of the values of Table I. would correspond in this analysis to a representation of the specific heat of solids by a Planck-Einstein function. At higher temperatures the deviations from the Debye function are not important. In this region a comparison between theory and experiment should be possible without further assumptions, *e.g.*, with the measurements on Ne and A. We do not now discuss the Ne values because more recent measurements have shown that the neon used by Clusius [4] was very impure. In Fig. 3, we show for argon the curves calculated for $a = 10$ and 40. The crosses are the measurements of Hauck.[5] There is really no agreement ; the experimental values decrease more with temperature than theory predicts. Moreover since the extreme calculation of Damkohler gave only a negligibly greater temperature dependence, one must conclude that with argon some other phenomenon occurs which our model does not consider. We are finally driven to the explanation already given by Eucken and Seekamp [9] that in the neighbourhood of the melting-point a weak association must still be active. With Hg a similar effect was found

* The molecular diameters calculated from the Sutherland constants afford a first approximation, and give an upper limit to d^1. A correct estimate is obtained fairly accurately by fitting the observed values to the theoretical curves.

by Magnus [6] and was quantitatively worked out. Similarly Na shows probable values > 6 cals. for C_v (also attributable only to association),* which must thus be taken into account in all the monatomic liquids so far considered.

For the same reasons that the Planck-Einstein function decreases more rapidly than the Debye function one must expect that our calculated curves for free oscillators also decrease more rapidly than those measured. Fig. 4 shows that this is actually the case. The C_v curves as functions of kT/B for the parameters $a = 1$ and 2 are drawn from the values of Table I. In addition the measured values for He (×), H_2 (○) and D_2 (+) are also plotted. For He, the $a \approx 1$ curve and for H_2 and D_2 the $a \approx 2$ curve qualitatively reproduce the measured results; the height and especially the position of the maximum fall correctly on the temperature axis.

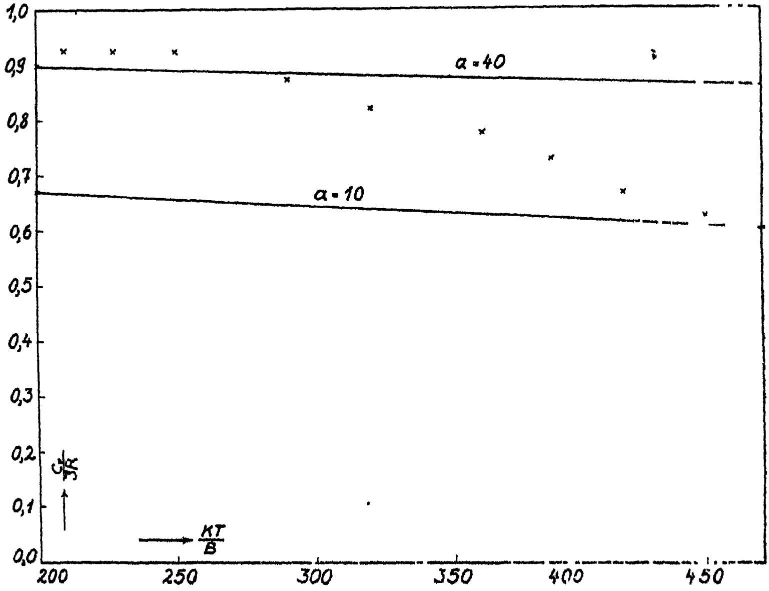

FIG. 3.

There are, however, quantitative deviations from the theoretical curves, in the same direction as the deviation of the Debye from the Planck-Einstein function. We therefore encounter the problem of calculating the spectrum of the coupled oscillators in liquids. Now a direct substitution of the Debye law $dZ = \nu^2 d\nu$ to the problem of liquids is impossible if the model of the harmonic oscillator is departed from. The Teller-Pöschl potential does not give a constant frequency for the free oscillator, which could be substituted in the formula.

On the other hand it should be possible to apply to liquids the Born-Karman method of calculating the C_v of solids. According to the Born lattice theory, the wave-length of a possible wave in a crystal depends only on the separation of two equivalent lattice points. But the corresponding quantity in the Teller-Pöschl potential is the box width d_0 which is given for each free oscillator. The evaluation of the Born formula, however, fails even with simple crystals. With liquids an attempt at calculation appears hopeless.

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* Jellinek (*Lehrb. physik. Chem.* IV., Stuttgart, 1933, p. 600) can only account for the equilibrium: $Ba + 2NaCl = BaCl_2 + 2Na$, if he assumes that Na occurs in the melt as Na_2.

There is now no other alternative but to carry through a rough approximation taking the coupling into consideration. Before the discovery of the Debye formula, Nernst and Lindemann[13] had succeeded in reproducing satisfactorily at not too low temperatures, the specific heats of solids by the sum of two Planck-Einstein functions, treating a part of the molecules as if it possessed twice the frequency of the rest. We have therefore made calculations analogous to the case of the free oscillator, with doubled d_0 values for $\frac{1}{4}$ of the molecule. In this way we obtain the dotted curve in Fig. 4, for $a = 1$ and 2. These curves reproduce the C_v values of H_2 better than one might expect from the rough approximation involved. The agreement is also better for He, although these curves fall too quickly, like the Nernst-Lindemann curves at low temperatures. The lower the temperatures, the more do the long waves of the spectrum increase in weight, thus diminishing the value of the calculation with two d_0 values. From this standpoint, the Teller-Pöschl potential without the additional assumption of association, reproduces the specific heats of H_2 and He correctly.

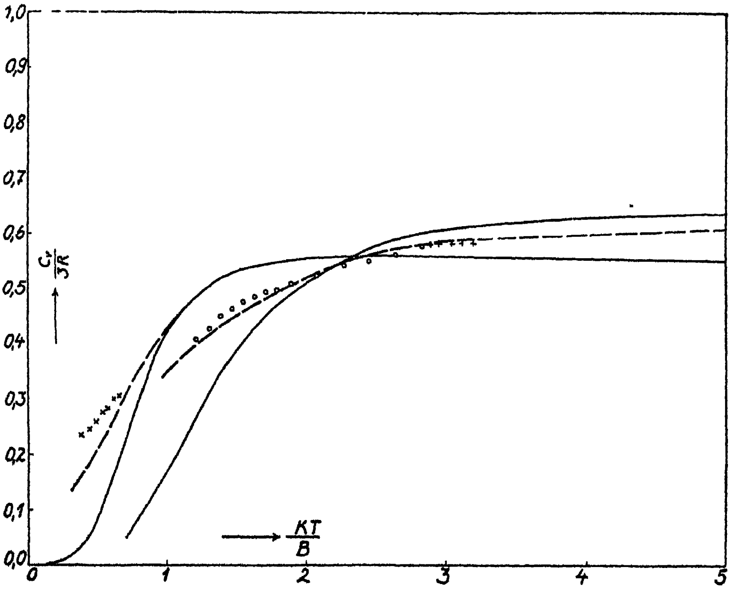

FIG. 4.

Closer inspection, however, particularly of the He values, shows that, with exact treatment of the coupling between the oscillators, the discrepancy between theory and experiment cannot quite be explained. Every curve through the measured values has an additional bump at zero. Even with He a slight association must be assumed in the liquid phase. Quantitatively it is not possible at present to separate it fro coupling, when this is treated by a rough Nernst Lindemann law.

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[13] W. Nernst and F. Lindemann, *Ber. Ak. Wiss. Berlin*, 1911 13. 494.

If association is present in all substances it is not evident why hydrogen alone should occupy an exceptional position. We consider it probable then, that the coupling effect is weaker for hydrogen than has been assumed in calculating Fig. 4, and that the deviation of the curve of the free oscillator is due, at least in part, to association.

Summary.

(1) From older theories of the C_v values of monatomic liquids, it follows that the motion at low temperatures is similar to the vibration of a solid body, while at high temperatures it changes into free translation.

(2) A potential investigated by Teller and Pöschl fits these assumptions. The C_v curves for this potential are calculated.

(3) Comparison with experiment of the curves so calculated show that this law describes the motion in a qualitatively correct fashion throughout their whole temperature range. For all liquids it is necessary, in addition, to take account of association.

We are indebted to Dr. Schäfer and Mr. Nonnenmacher for their help in the laborious calculations.

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ON THERMAL AGITATION IN LIQUIDS.

By Leon Brillouin (*Collège de France, Paris*).

Received 21st September, 1936.

The nature of thermal agitation in solids or in gases is now well known, but there still remains some uncertainty as to the nature of thermal agitation in liquids; this problem is of course closely connected with the question of liquid molecular structures. I want to introduce some remarks from a purely theoretical point of view,[1] and to discuss a sort of "ideal liquid"; the comparison of this ideal liquid with actual liquids is of interest, and brings forth some valuable information.

I start from Debye's theory of specific heats for solids, thus first treating the solid or liquid as a continuous medium, and afterwards introducing a limitation of the number of degrees of freedom due to atomic structure. In a solid body, we have two elasticity coefficients λ and μ, and two types of elastic waves, namely longitudinal and transverse waves. Born's famous researches on vibrations of crystal lattices showed that both waves have the same minimum wave-lengths, but different maximum frequencies, according to the difference in wave velocities. Let us consider a monatomic crystal lattice, built up of N atoms; there will always be N degrees of freedom for longitudinal vibrations and $2N$ for transverse vibrations. If these vibrations are harmonic, the total energy at temperature T is twice the kinetic energy $E(T) = 3RT$ thus yielding a specific heat.

$$c_v = 3R \qquad (1)$$

at high temperatures.

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[1] L. Brillouin, *J. Physique* (7), 1936, 7, 153.

Let us now suppose the rigidity coefficient μ to decrease and tend to zero; we pass from the solid body to a sort of ideal liquid, with a compressibility defined by the λ coefficient. Elastic longitudinal waves can still be propagated, and are always N in number, but what about the $2N$ degrees of freedom of the transverse type? There are no more transverse waves, and it is easy to see that these sorts of motions will degenerate into whirl systems, for which there is no potential energy, but only a kinetic energy $\frac{1}{2}kT$ per degree of freedom. This yields a first contribution NkT to the thermic energy.

For the N longitudinal waves, we shall find an energy $E_l(T)$ equal to NkT if the vibrations are still sinusoidal, and differing from this value for other types of non-sinusoidal vibrations, *e.g.*, those studied by Eucken. The total energy would thus be of following type

$$E(T) = E_l(T) + RT \approx 2RT \quad . \quad . \quad . \quad (2)$$

when $c_v \approx 2R$

As a matter of fact, actual liquids show a specific heat always greater than $2R$, as results from curves drawn by Bauer and Magat; the limit $2R$ seems to be obtained regularly at the critical point.

These deviations might be related to following causes:—

1. Non-sinusoidal longitudinal waves, as supposed by Eucken, with the difference that Eucken treats all the $3N$ degrees of freedom on the same footing, while I insist on first eliminating $2N$ degrees of freedom for rotational internal motions.

2. Possible existence of ultra-microscopic solid clusters, with two results:—

(i) Transverse motions of very small wave-lengths, near the Born-Debye limit, could still take place, and a corresponding term of potential energy should be introduced.

(ii) There would be a heat of fusion term to introduce, due to the progressive fusion and disappearance of these solid clusters when the temperature is raised.

The point I want to emphasise is the transformation of the $2N$ transverse waves into internal rotational motions, which seems to be inevitable from the theoretical considerations which I have developed.

Some valuable information as to the thermal agitation and the structure of liquids should be obtained from a detailed study of the structure of the Rayleigh scattered light.[2] I have shown that elastic waves give a doublet with some well-defined relations to the angle of scattering and wave velocities; on the other hand, cluster formation would yield a central line of unperturbed frequency, and whirl systems should give a broadening of this central line. Actual liquids always show the triplet formed by the central line and the doublet, but the relative intensities of these three components seem to depend very much upon the temperature and the nature of the liquids, but it is perhaps too early yet to draw precise conclusions from these experiments.

*GENERAL DISCUSSION.**

Dr. E. Bartholomé (*Göttingen*), discussing Professor Brillouin's paper, said: Our work, and that of Professor Brillouin, involves two effects which must be borne in mind in any complete theory of liquids, but unfortunately the unification of the two points of view is not yet possible.

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[2] L. Brillouin, *Jubilé Marcel Brillouin* (Gauthier Villars, Paris), 1935, p. 213.

* On the two preceding papers.

Experiment must, therefore, decide which effect is the more important in real liquids. For hydrogen and helium the measurements of Eucken show clearly that the limiting value of C_v at high temperatures is 3 cal., and there is no evidence that for other liquids the value is 4 cal.; it must, however, be remembered that this value is not a necessary consequence of coupled vibrations of the molecules. Apart from the conception of harmonic vibration, the value of 3 cal. is obtained without further ado from the concept of coupled oscillations. If, then, we consider thermal vibration at low temperatures, the observed specific heat is quite different from that predicted by our theory. We show that this deviation is qualitatively of the same nature as the deviation of the Debye curve from the Planck-Einstein equation. At higher temperatures, however, the two curves tend to coincide. In framing a theory which will fit in as closely as possible with experiment, we consider it essential to represent the vibrations of liquids as oscillation with constant amplitude, whilst the wave theory requires only a correction at low temperatures.

Dr. M. Magat (*Paris*) said: The example given by Mr. Bartholomé against the theory of Professor Brillouin seems to be not quite proved. Indeed both in solid He, as in H_2 and D_2, the equipartition temperature is not yet reached, *i.e.*, their specific heat at melting-point is smaller than 3 k.cal. For this reason quantum effects still play a part in the liquid state.

Mr. J. D. Bernal (*Cambridge*) said: Professor Brillouin's theory suggests a general explanation of the shape of the specific heat curves of a liquid between the melting-point and the critical point. Some such gradual breakdown of transverse vibrations as he postulates must occur. I do not feel, however, that there is any necessity to postulate cluster formation to account for the deviations from his theory. The type of irregular but homogeneous configuration which I put forward in my theory would, at any rate qualitatively, be able to produce the same effects as clusters, against the existence of which there are considerable theoretical and experimental objections. As the interchange of configurations at any given temperature would not be infinitely rapid but would occur at a rate very much slower than that of the normal thermal vibrations, transverse motions of high frequency should be possible, though the frequency limit would get greater and greater the higher the temperature. In the second place, the heat fusion term which he introduces would, from this point of view, be due, not to the break up of clusters, but would simply be the configurational term of the specific heat.

Professor Eucken's theory of specific heats of liquids can only be considered as part of a more general theory of liquid specific heat. It takes as its fundamental assumption the temperature independence of the configuration of the liquid. With this assumption the theory of the specific heat of liquids must clearly be some compromise between that of the theory for crystals and for gases. Any such theory must, however, always lead to values of specific heat of less than $3R$, whereas that for many liquids is appreciably greater. The theory will only show any approximation to the real state of affairs at very low temperatures, where zero point energies play a large part. The greater part of the difference between the specific heat of the liquid and that of the crystal is due, in the case of ordinary liquids near the melting-point, to a breakdown of the simple harmonic vibrations into more complicated forms.

Professor M. Born (*Edinburgh*) said: The general feature of all theories of liquids is the assumption that the molecular state of a liquid is something between a crystal and a gas. The question arises: what quantitative relation holds between the ordered and the disordered component of the molecular motion? A phenomenon which may give some information (the theory of which has been given by Professor Brillouin himself in some earlier papers) is the displacement of spectral lines scattered by liquids and solids, due to the Doppler effect. If the incident beam is monochromatic, the light scattered by a perfect crystal in a given direction should consist of two fine lines at equal distances on both sides of the incident line. This follows when the scattering is considered as a diffraction of the incident beam by a set of sound waves which act as a grating. The direction and wave-length of these waves are fixed by Bragg's condition and, since there are two such waves moving in opposite directions with equal velocities, the incident line is split by the Doppler effect into two components. Observation has confirmed this prediction. But in liquids there appears rather strongly also the undisplaced line. This seems quite natural from the standpoint that the molecular motion in liquids cannot be described completely as a superposition of sound waves, but has a disordered, gas-like component. Measurement of the relative intensities of the undisplaced line and the two Doppler satellites should, I feel, present a method for estimating the ratio of these two parts of molecular motion. Can Professor Brillouin say whether this attractive idea of his has been used for the purpose indicated, and what results have been obtained ?

Professor L. Brillouin (*Paris*), in reply to Professor M. Born, said : The predictions of my earlier theory[3] seem to accord pretty well with experiments on light scattering by solid bodies (experiments on quarts by Gross, for instance). An incident monochromatic beam of frequency ν_1 is found to give, by scattering, a doublet $\nu_1 \pm \nu$, where the frequency ν may be calculated from the sound velocity and angle of scattering. In liquids, most experimenters have found in the scattered radiation a triplet ν_1, $\nu_1 \pm \nu$, and also further lines of the type $\nu_1 \pm \nu'$, where ν' may correspond to rotation motions of the molecules. A summary of these problems will be found in the article quoted in my paper ;[4] the most interesting point for experimental work, should be a detailed investigation of the influence of temperature on the relative intensities for the different scattered lines.

Dr. F. London (*Paris*) said : The model calculated by Professor Eucken and Bartholomé shows a considerably slower decrease of the specific heat (with increasing temperature) than found by experiment. This seems to indicate that actually the curvature of the potential minimum becomes flatter with increasing molecular motion.

Dr. E. Bartholomé (*Gottingen*), in reply, said : Dr. Magat's objection is not valid ; the specific heats both of He and of H_2 are measured far below the critical temperature. In both cases C_v passes through a maximum not much over 3 cal. and falls towards 3 cal. ; this appears to be the limiting value at higher temperatures. Obviously the behaviour at lower temperatures is to be attributed only to quantum effects. The advantage of our theory, however, is that it is applicable both to the classical and the quantum aspects. Professor London's explanation of the unusually rapid fall of C_v at higher temperatures is of course not excluded. Since the " diffusion process," however, only explains a too rapid fall at high temperatures, and we have, at any rate in the case of helium at low temperatures, a too rapid rise of specific heat, it follows that we are concerned with the effect which we call " association," but Bernal more accurately calls " configuration variation." Which effect preponderates cannot yet be said, since neither has as yet been quantitatively worked out.

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[3] *Ann Physique*, 1921, **17**, 88.

[4] *This vol.* p. 55, *loc. cit.*[3].

ON THE LIQUID STATE AND THE THEORY OF FUSION.

By J. Frenkel (*Leningrad*).

Received 27th July, 1936.

I. Heat Motion in a Liquid; Connection between Fluidity and Rigidity.

It has been usually assumed, especially since the appearance of Van der Waals' theory, that the liquid state of matter is more akin to the gaseous than to the solid crystalline state, amorphous solids being considered as "supercooled liquids." Although deprived of a regular structure characteristic of the solid *crystalline* state, an amorphous solid is still a solid rather than a liquid from the point of view of its mechanical properties, for it possesses a *rigidity* of which the liquid is supposed to be deprived. Limiting himself to amorphous bodies, Maxwell has shown that "rigidity" and "fluidity," which are considered respectively as characteristic of the solid and of the liquid state, are properties which are not mutually exclusive but can coexist in the same body. The ratio of the viscosity coefficient η to the modules of rigidity N represents a certain time τ, the "relaxation period" of the body; when this time is very small (*e.g.* at high temperatures) the body behaves as a liquid, practically devoid of rigidity; when on the contrary it is very large, the body behaves as a solid, practically devoid of fluidity.

Maxwell's "relaxation theory of elasticity" is purely phenomenological. A molecular or kinetic theory, practically equivalent in its implications to that of Maxwell, was first proposed by the author in 1926.[1] It is based on the fact that liquids at low temperatures (near the crystallisation point) have a *specific heat of the same magnitude* and even usually somewhat larger than the *corresponding crystalline solids*. This means that the heat motion has in both cases approximately the same oscillatory character. It has been usually assumed that in a crystalline solid the atoms (or molecules) oscillate about relatively *fixed* equilibrium positions. That this is not exactly true is shown by the phenomena of *diffusion* in crystalline solids or of conduction of electricity in ionic crystals. In order to explain these phenomena one must assume that the equilibrium positions, about which an atom oscillates, is switched from time to time from one place to another at a distance δ of the same order of magnitude as the interatomic distance. In the case of crystalline solids this implies a certain amount of *dissociation* of the lattice, whereas in amorphous bodies the dissociation can be regarded as complete.

The heat motion in an amorphous body—liquid, say—is therefore neither a simple translatory motion as in an ideal gas, nor a simple oscillatory motion as in an ideal solid. It has both the character of an oscillation and of a translation being in fact an oscillation about an equilibrium position, which is not fixed but performs a jerky translatory motion, being switched now and then to a distance equal on the average to δ. It can easily be shown that the average time τ between two consecutive switches (or more exactly the average longevity of a given equilibrium position) is a rapidly decreasing function of the temperature, namely

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[1] *Z. Physik.*, 1926, **35**, 652.

$$\tau = \tau_0 \, e^{U/kT} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where τ_0 is the period of the oscillations ($\sim 10^{-13}$ sec.) and U a certain "activation energy," corresponding to a transition from one equilibrium position to the next one ($\sim$ a few thousand calories per mol.)

The quantity

$$D = \frac{\delta^2}{6\tau} = \frac{\delta^2}{6\tau_0} e^{-U/kT} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

is the diffusion or more exactly the self-diffusion coefficient of the body (solid amorphous or liquid). Using Einstein's relation $Df = kT$ between the diffusion and the friction coefficient (f) and treating each atom or molecule as a small sphere (radius $a \cong \delta$) to which Stoke's law can be applied, that is putting $f = 6\pi\eta a$, where η is the viscosity coefficient of the body, I derived for this coefficient the expression

$$\eta = \frac{kT\tau_0}{\delta^2 a} e^{U/kT} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which represents more or less accurately the temperature dependence of viscosity. It should be mentioned that $1/\delta^2 a$ is approximately equal to the number of atoms (or molecules) in unit volume n. The quantity $\frac{kT}{\delta^2 a} = nkT$ is thus equal to the pressure p which these atoms would exert if they formed a gas. The relation (3) is thus similar to Maxwell's formula, if the rigidity modulus N is replaced by the fictitious hydrostatic pressure $p = nkT$ and if $\tau = \tau_0 e^{U/kT}$ is identified with the relaxation time of Maxwell's theory.

This identification seems quite natural, since the molecular basis of the relaxation phenomena must obviously consist in a ***rearrangement*** of the atoms, or more exactly of their equilibrium positions, thus relieving the stresses which tend to produce the rearrangements, or more exactly systematic rearrangements of a given type (corresponding to viscous flow). In fact, random rearrangements take place in the absence of external forces, their effects being on the average mutually cancelled. In the presence of such forces, rearrangements of one type are more favoured than those of other types, which results in an observable rearrangement corresponding to the phenomenon of flow (we meet a quite similar situation when we consider the motion of ions in a solid or liquid electrolyte in the presence of external electrical forces).

Replacing the fictitious hydrostatic pressure $p = nkT = \frac{kT}{\delta^2 a}$ of formula (3) by the rigidity modulus N of the body, we obtain the following expression for the visocsity coefficient

$$\eta = N\tau_0 e^{U/kT} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

which gives a fairly good agreement with the experimental data if N is assumed to be independent of the temperature, *i.e.* if we attribute to the liquid a rigidity of the same magnitude as that of the corresponding solid.*

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* An expression of the form $\eta = Ce^{U/kT}$ was derived by Andrade in 1930 by an argument of a rather qualitative character which is substantially equivalent to mine (see *Nature*, 1st March and 12th April, 1930).

It should be mentioned that the value of the constant C calculated from (4), *i.e.* $C \quad N\tau_0$ comes out too large Since τ_0 cannot be smaller than 10^{-13} sec, this discrepancy can be removed by assuming for a liquid a rigidity coefficient N about 10 to 100 times smaller than for the corresponding solid

The above considerations refer pre-eminently to a mono-atomic body (although such bodies have not been obtained hitherto in the solid amorphous state). In the case of a liquid body, with relatively simple molecules, one must take into account not only the vibration and translation of the centre of gravity of the molecules, but also their *rotation* about this centre of gravity. At low temperatures this rotation must have an oscillatory character, the equilibrium orientation being switched rather rarely from one direction to another, whereas at high temperatures it must approach to the free rotation characteristic of a gas.

Debye has recently attempted to apply this picture of the rotation motion of the molecules in polar liquids to the calculation of their dielectric constants. I have shown, however, that his new theory was inconsistent with this picture, its basic assumption being actually the existence of *fixed* equilibrium orientations (just as in an ideal solid) and the reason for its agreement with the experimental data lying in the inapplicability of the ordinary relaxation theory to the rotation motion of simple molecules. In fact, the relaxation theory, such as Debye's old theory of the polarising action of an alternating electric field, applies only to those cases in which the elementary switches of the equilibrium orientation are small, whereas with simple molecules they can be quite large.[2]

Summing up, we can say that the heat motion in a liquid body at low temperatures (near their crystallisation point) approximates to that of a solid, being essentially an oscillatory motion, of the same type as in an ideal solid. With increase of temperature this oscillatory character is gradually lost, the average number of oscillations about *the same* equilibrium position (or orientation) decreasing as $e^{U/kT}$. At high temperatures (near the critical one) the oscillatory character must practically vanish, the heat motion of the molecules approaching to free translation or free rotation in a gas—as evidenced by the fact that the specific heat of liquids at high temperatures approaches that of the corresponding gases.

II. Regularity of Structure and its Dependence on the Volume.

Although from the point of view of the heat motion and the resulting properties—mechanical and thermal—the liquid state can be considered as intermediate between the gaseous and the solid one, getting more and more "solid-like" as the temperature is lowered, yet from the point of view of *structure* there seemed to remain between the liquid and the solid crystalline state a gap that cannot be bridged by any kind of continuous transition.

We now know that this is not so. In the first place a certain lack of regularity is found in crystals at high temperatures, near the melting-point, a portion of the atoms being as it were "internally evaporated" or "dissolved" in the lattice, and a portion of the lattice points being left vacant.[3] In the second place a certain amount of regularity is still found by X-ray analysis of liquids, especially in the neighbourhood of the crystallisation point. As has been shown by Kratky[4] the X-ray diagrams of simple substances in the liquid state can be explained by assuming any atom to be the centre of a crystal lattice with a somewhat "diffused structure." This means that the atoms, surrounding the initial one (which can be chosen at random), are not found in the corresponding lattice points, as would be the case with an ideal crystal, but are displaced with respect to these points by an amount whose average value increases as the square root of the distance from the initial atom. The displacements which are due to the heat motion and whose average value does not change with the distance, are here not taken into account. The ratio

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[2] See J. Frenkel, *Acta Physicochimica, U.R.S.S.*, 1936, **4**, 341.

[3] *Cf.*, for example, *ibid.*, 567.

[4] *Phys. Z.*, 1933, **34**, 482.

$$\frac{\overline{\xi^2}}{6r} = \Delta \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where r denotes the distance of the given atom from the initial one and ξ its displacement from the corresponding lattice point, can be defined, by analogy with ordinary diffusion, as the " structure diffusion coefficient of the liquid." The distribution of the displacements ξ for a given value of r about the average value $\sqrt{\overline{\xi^2}}$ must be described by Gauss' law.*

The " structure diffusion coefficient " Δ is a function of temperature, not yet investigated quantitatively, but certainly increasing with T, tending towards a certain limiting value which corresponds to complete disorder. The opposite case of complete regularity could be described by putting $\Delta = 0$. It is, however, fairly clear that the above description cannot be applied to such cases when the degree of irregularity is small, as for example in a crystal near the melting-point. Here the irregularity is due not to small displacements of all the atoms but to large displacements of a few (" dissociated ") atoms. A characteristic difference between such " quantum-like " irregularity and that assumed in Kratky's work, is that the former does not affect the long distance regularity of structure, whereas the latter absolutely excludes it, although in a small volume it represents, in principle, but a relatively small distortion of the crystal lattice.

It still therefore remains questionable whether one can pass from the absolutely regular structure of a crystal, to the absolutely irregular structure characteristic of a liquid at high temperatures, or rather of a gas, by some kind of a continuous transition.

Such a transition can be found in a *gradual expansion of the body* (by application of a uniform negative pressure to its surface) at any given temperature. The tendency of the atoms to be arranged in a regular crystal lattice must be restricted, at least at low temperatures, to the case of positive pressures. If the lattice constant is increased by a sufficient amount—doubled, say—the regular arrangement will no longer correspond to the minimum of potential (or free) energy, and the atoms will tend to coalesce into separate smaller aggregates of two or more, which means a complete disruption of the body. If the atoms are assumed to be at rest (which as a matter of fact cannot be the case even at the zero point of temperature), then the disruption of the body must actually take place at much smaller expansions (corresponding to a linear dilatation of about 10 per cent.), the regular structure remaining stable until the breaking point is reached.

The situation is substantially changed when the heat motion of the atoms is allowed for. In this case the tendency towards a regular arrangement can be *locally* lost at relatively very small expansions of the body as a whole, this tendency being determined not by the *average* expansion, but by the local expansion of the crystal lattice near the atom under consideration.

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* This circumstance has been pointed out by Lashkarew in an unpublished paper, whereas Kratky assumed for the sake of simplicity a linear distribution.

This argument can also be put in another form. The dissociation of the atoms from the lattice points requires a certain activation energy, which is decreased with increase of the volume. Consequently, with a sufficiently large expansion we may obtain a large degree of dissociation even at relatively low temperatures. When, however, the dissociation of a crystal becomes very large, it can no longer be used as a picture of the resulting arrangement and Kratky's picture of a diffused arrangement must be substituted for it.

I have not found yet a general method of describing the gradual decrease of regularity which would merge into the dissociation method for small and the "structure diffusion" method for large degrees of irregularity. It is possible that here, just as in the Bragg-Williams-Bethe theory of the solid solutions, two types of order should be distinguished: a long distance regularity, which can persist in spite of local distortions, and a short distance regularity which can persist in the absence of any long distance correlation. It is perhaps possible to say that a liquid (or, in general, amorphous) body can be distinguished from the corresponding crystalline solid by the absence of long-distance regularity, the short distance regularity still existing in the liquid and only gradually vanishing with increase of temperature or of the volume.* It would, however, be erroneous to think that the process of melting can be simply reduced to the loss of long distance regularity; in this case the melting-point would correspond to the Curie point of ferromagnetic substances, whereas in reality it is determined by the thermodynamic equilibrium of the two states—solid (crystalline) and liquid.

III. The Theory of Fusion and Crystallisation.

The arguments of the preceding section strongly support the view, that the transition from the solid crystalline state to the liquid one can be carried out in a continuous way by gradually increasing the volume of the body at a constant temperature (instead of heating it at constant pressure as usually done). We shall not discuss here the practical possibility of this process, which is connected with the application of negative pressure of sufficiently large amount.†

The main point for us is that with increase of volume the regularity, characterising the initial crystal, will gradually decrease until we finally obtain an amorphous body; whether the latter will be solid or liquid must depend upon the temperature.

This picture seems at first sight to be in complete opposition with reality, since in reality the transition from the solid crystalline to the liquid state, obtained either by raising the temperature, or by increasing the volume (for normal substances, initially compressed) is a *discontinuous one*. This discontinuity can, however, be interpreted in the same way as that which is observed in the transition from the liquid to the gaseous state. According to the Van der Waals' theory it is due *not* to some fundamental qualitative difference between the two states, but to the mechanical (or thermal) instability of the intermediary states of the corresponding homogeneous body, this instability being revealed by the characteristic shape of the isotherms. Now it can easily be shown that the isotherms (p, v) corresponding to a continuous transition of a body from the solid crystalline to the liquid state, must, in general, display the same characteristic shape as those of the Van der Waals' theory, though for quite different reasons, and in entirely different temperature regions.

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* I am indebted for this remark to my co-worker, T. Kontorova.

† It should be mentioned in this connection that liquids can resist a very high negative pressure without breaking up.

The nearest approach to this result is found in a recent paper by Hertzfeld and Göppert Mayer,[5] who investigated theoretically the isotherms of ideal crystals of argon and helium and found that at sufficiently high temperatures the pressure does not monotonically decrease with increase of volume but passes through a minimum. They attempted to identify this minimum with the fusion point and did not investigate the behaviour of the isotherm beyond it. Now, assuming the crystal to preserve its ideal regularity, the pressure is found to increase up to infinity at the breaking-point, after which it suddenly falls to a very small value. As we have mentioned before the regular structure becomes statically unstable beyond the breaking-point. It must, however, become dynamically unstable (with due account to the heat motion) long before it is reached. It is clear that the gradual loss of regularity of the body with increasing extension must arrest the increase of pressure beyond the minimum, and lead to a finite maximum, accompanying the latter and corresponding to a volume much smaller than that of the breaking-point (*cf.* the full curve of Fig. 1, the dotted curve referring to an ideal crystal). We thus obtain exactly the same type of isotherm as in Van der Waals' theory. The actual transition solid (crystalline)–liquid must take place not along this wave-like isotherm but along the straight line ABC which cuts from it two segments of the same area and which corresponds to the breaking up of the homogeneous body into two phases—the solid one at A and the liquid at B.

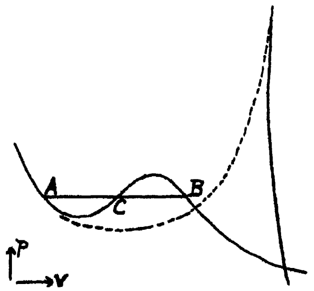

FIG. 1.

The quantitative theory of the above transition is still very unsatisfactory, as we have no equation of state capable of describing both the crystal and the liquid with the same approximation as is done by Van der Waals' equation for the liquid and gaseous states. We can hardly go beyond the results of Hertzfeld and Göppert Mayer, in explaining the rise of the pressure in a certain range of increasing volume. From the molecular point of view this can be explained by the fact that the asymmetrical character of the force which holds an atom in equilibrium near its neighbours is enhanced when their average distance apart is increased. Under purely symmetrical forces the heat motion of the atoms would not be accompanied by expansion and consequently would not produce any pressure. Assuming the average oscillation frequency ν to be a (decreasing) function of the volume, one obtains for the thermal pressure of a solid the expression

$$p = -3RT\frac{\partial \lg \nu}{\partial v} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which is proportional to the (absolute) temperature and increases with the volume. Now, this decrease of ν with increase of v, the oscillations being assumed to remain harmonic, is dynamically equivalent to the anharmonicity, due to the non-linearity of the forces holding each atom in its equilibrium position. It follows from the preceding expression that at sufficiently low temperatures the thermal pressure becomes insufficient to produce a temporary increase in the resulting pressure as a function of the volume. At and *below* this "critical temperature" T_1, the (p, v) isotherms will therefore be monotonically falling curves of the same type as the Van der Waals' isotherms at and *above* the ordinary critical point T_2. We thus see that fusion and crystallisation can take place in the usual discontinuous way only *above* a certain critical temperature T_1; below this temperature we must expect to find a perfectly continuous transition from the crystalline to the amorphous state (whether the latter will be "liquid" or "solid" depends upon the value of T). Since T_1 is low, such transitions must probably take place in regions of negative pressures only; that is why they have not been observed hitherto. If it were possible to expand a metal below its critical fusion temperature, we should probably obtain it in a *solid* (and not liquid) amorphous state, which perhaps could be preserved as a "supercooled" state after the release of the pressure. The failure of the attempts to obtain metals and other simple bodies in the solid amorphous state are probably due to the fact that they have been investigated at temperatures above the critical fusion temperature.

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[5] *Physic. Rev.*, Dec. 1934.

According to our views the liquid state is in all respects intermediate between the solid (crystalline) and the gaseous one and can be, in principle, connected with them by continuous transitions, involving, however, unstable intermediate states and therefore replaced by discontinuous transitions above the fusion critical temperature or below the Van der Waals' vaporisation critical temperature. The ordinary discontinuous fusion does not mean a transition from the regular crystalline state to the irregular amorphous one. Although devoid of the long distance regularity characteristic of the crystal (and vanishing for some *intermediate* state), it still possesses near the melting-point a high degree of short distance regularity, which is gradually lost with increase of temperature. This, by the way, explains why the specific heat of liquids is greater than that of the corresponding crystals near the melting-point. The "partial amorphisation energy" which is manifested in the form of latent heat at melting is manifested above it in the higher value of the specific heat, distributed over a fairly large temperature interval.

The preceding considerations require a certain extension in the case of more complicated substances. Thus, for instance, in the case of a di-atomic substance like HCl, two types of irregularity must be taken into account: the irregularity in the positions of the centres of gravity of the molecules, and the irregularity in their *orientations*. The transition from a state with nearly complete regularity in the distribution of the orientations, to a state with a relatively small regularity in their distribution at small distances and no regularity whatever at large distance—a transition which we shall call "orientation fusion"—can here take place at a temperature below that of ordinary fusion and having a mechanism of the same type (*i.e.* involving unstable intermediate states) as the latter. Owing to the presence of impurities such transitions may lose their discontinuous character and may be characterised by anomalies in the specific heat curves of the corresponding substances (like NCl, CH_4, etc.).

With still more complicated substances intermediate states can appear which are found in the nematic and smectic phase of liquid crystals.

I think it highly probable that here, too, we have to do with transitions which are discontinuous only in view of the instability of the intermediate states.

The theory of the virtual continuity between the solid (crystalline) and liquid states gives a key to the understanding of the kinetics of the crystallisation process, the crystallisation centres being present, in a certain sense, far above the crystallisation point. It would, however, be premature to discuss this question at the present time.

ON THE RANGE OF STABILITY OF THE FLUID STATE.

By F. Simon.

Received 5th August, 1936.

In this paper I discuss in outline the conclusions to be drawn from experimental facts as to the stability range of the fluid state. Detailed discussion will be published later.

By the term "fluid state" I include both gas and liquid. If the liquid state proper is defined by the part of the p-T diagram situated below the critical temperature and above the equilibrium pressure with the gas but below that with the solid, then this state, as will be seen later, has only a very restricted range of stability, and the only relevant point to discuss concerning the liquid state proper is the behaviour at the lower end of the temperature scale.

In general the liquid state is limited by solidification at the triple point, but many liquids can be supercooled and can still exist in internal equilibrium,[1] although unstable compared with the solid phase. The supercooled liquids pass with falling temperature into the vitreous state. These vitreous states are no longer in internal equilibrium; [1] in other words, an infinite number of different states are present and the system can not be treated thermodynamically.

By cooling down very slowly below the temperature range of vitrification it should be possible to attain the state of equilibrium at any temperature. In this case the substance should, without crystallising, pass into an ever-increasing state of internal order,[1] and finally at absolute zero reach the state of perfect order. This state, which I have called "liquid degeneracy" [2] cannot be realised experimentally in a normal liquid because of the vast length of time which would be necessary, and would on the one hand be impracticable and on the other hand, moreover, allow the substance to pass into the more stable state of the crystal.

One liquid exists, however, which is even stable at the lowest temperatures, *viz.* liquid helium. It has been explained by Bennewitz and Simon [3] and by Simon [4] that the cause of this anomalous behaviour is the huge amount of zero-point energy present in the condensed helium.

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[1] F. Simon, *Ergebn. exact. Naturw.*, 1930, **9**, 247 ff.; *Z. anorg. Chem.*, 1931, **203**, 219.

[2] F. Simon, *Z. Physik.*, 1927, **42**, 806.

[3] K. Bennewitz and F. Simon, *ibid.*, 1923, **16**, 183.

[4] F. Simon, *Nature*, 1934, **133**, 529.

In this case then, we have a liquid which at absolute zero will be in a state of perfect order. Actually this passing into the ordered state happens for the most part in a rather restricted temperature range (that of the λ-phenomenon) and all the observations on entropy, heat conduction and viscosity indicate that the conception of liquid helium below the λ-point as a liquid in a state of order is correct, and that on cooling it down still nearer to absolute zero one should expect no appreciable changes in its behaviour, such as passing into the vitreous state or becoming unstable compared with a crystalline form.

Investigation of the properties of liquid helium has already resulted in a better understanding of the nature of the liquid state, and further investigations will be valuable, as one can study in this case the properties of a liquid from the very beginning. For our present purpose however, we merely record that a liquid can still exist at absolute zero, and further, that a liquid may in certain cases not exist at all.

As already indicated, much of the lattice energy of liquid helium (more than 80 per cent.) is compensated by the zero-point energy. Consider now the case of the lighter isotope of helium, He^3; here the potential of the intermolecular forces is exactly the same as for the normal helium. The zero-point energy, however, increases (at a given volume) as the inverse square root of the masses, or even, taking London's [5] treatment of liquid helium, as the inverse ratio of the masses themselves. Quantitative treatment, so far as available in the present state of theory, indicates that the zero point energy of liquid He^3 would probably be so large that it could not condense at all—it would be a real "permanent" gas. But in any case whether that is so, or whether it is just able to form a liquid phase, one can imagine systems, for instance He^2, where the zero-point energy would undoubtedly prevent condensation to the liquid state. This does not mean, of course, that this substance could only exist in the gaseous state, as one can force it into the ordered state of a crystal by external pressure.

This leads us to the more important point, namely whether it is possible to solidify substances at any temperature simply by applying high enough pressures.

Until a few years ago it was not possible to predict with certainty the slope of the melting curve at high temperatures. This is due to the fact, that it has a very steep gradient, so that with the pressures obtainable experimentally it cannot be traced up to very high temperatures, the limit being reached by solidifying some substances in the region of the critical temperature. As there is no well-founded theory on the equation of state of liquids, all possible suggestions have been made as to the continuation of the melting curve. Tammann extrapolated that it would bend round so that the crystalline state would have a very limited range of existence, and the fluid state would preponderate; Schames thought that it would become perpendicular to the T axis, reaching a limiting melting temperature; whereas Bridgman, from the many experiments he carried out at high pressures, thought that, though it would become steeper and steeper, it would never be perpendicular to the T axis.

In 1927 the author sought to replace the purely empirical formulæ by one with a better theoretical foundation, connecting the parameters of the melting curve with properties of the single phases. It was found

[5] F. London, *Proc. Roy. Soc., A*, 1936, **153**, 576.

that a quantity a, intimately connected with the internal pressure of the single phases, was the determining parameter and the following formula [6] was derived:

$$- 1 \Big] \quad . \quad . \quad . \quad . \quad (1)$$

(T_0 = normal melting temperature.)

It is obvious that extrapolating this formula to temperatures below T_0, *i.e.* to negative pressures,[7] has a physical meaning, and it is well worth noticing that as dp/dT vanishes at absolute zero, Nernst's theorem is fulfilled. It follows from (1) that to melt a substance at absolute zero a negative pressure of magnitude a must be applied.

In a paper with Glatzel [8] the existing experimental material was surveyed from the point of view of (1) which was found to represent experiment very well, and even warranted extrapolating the melting data from a short piece of the melting curve up to very high pressures and temperatures. Moreover the values of a derived from the melting data agreed very well with data derived for the internal pressures of the single phases by other methods, and the quantity c was of the same order of magnitude for nearly all substances, namely about 2.[9]

Since c is nearly equal for all substances, we can write (1) in the reduced form: [10]

$$p_r = T_r^{\,c} - 1 \quad . \quad . \quad . \quad . \quad (2)$$

(where $p_r = p/a$; $T_r = T/T_0$) and we can deduce from this that, to reach relatively very high temperatures on the melting curve with a given pressure, the substance must have a small a, *i.e.* have small intermolecular forces, or, in other words, a low boiling-point.

The author and his collaborators [11] therefore began research on the melting curves of the low boiling substances, especially helium and hydrogen. The prediction of the formula was fully verified, and relatively very high melting temperatures were attained, *e.g.* at 5600 atm.

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[6] This formula is identical with the form in which it was given originally: $\log (a + p) = c \log T + b$. See *Z. Elektrochem.*, 1929, **35**, 618.

[7] Liquids have even been subjected experimentally to appreciable negative pressures (see for instance, J. Meyer, *Abh. d. deut. Bunsengesellschaft*, 1911, No. 6).

[8] F. Simon and G. Glatzel, *Z. anorg. Chem.*, 1929, vol. 178, p. 309.

[9] Only the metals show higher values and these lie between 3 and 4.

[10] Statements concerning the "law of corresponding state" can, of course, never demand an absolutely strict validity, since all the individual properties of a substance cannot be expressed by a few parameters, and one would even expect these properties to play a greater rôle than in the case of the transformation liquid-gas. The reduced form given above seems, however, to be valid to the same extent as the corresponding formula of van der Waals for the vapour pressure curve where the constant f is not absolutely the same for all substances. For this transformation also, the metals do not show the same constants as those derived for the substances with van der Waals' binding forces, if an attempt is made to fit them into the "law of corresponding states."

a and T_0 are not absolutely independent of each other, so that for a lower degree of approximation one can even give a reduced melting formula with only one constant.

It should be added that in this paper we are considering only substances which behave normally, *i.e.*, those with a positive dp/dT; this is justified, as Bridgman has shown that, with increasing pressure, these abnormal substances undergo polymorphic transitions and then behave normally.

[11] F. Simon, M. Ruhemann and W. A. M. Edwards, *Z. physik. Chem.*, *B*, 1929, **2**, 340; 1929, **6**, 62; 1930, **6**, 331.

the melting curve of helium could be traced up to 42°, more than eight times the critical temperature.[12]

Since all the experimental data can be represented by a reduced formula, we may generalise the results [13] for the model substances, and state that the melting curve will become steeper and steeper, but will never curve back or reach a final melting temperature: in other words it will go on as Bridgman predicted, and we can exclude the possibilities envisaged by Tammann and Schames.

Thus both the fluid and the crystalline states occupy nearly equal parts of the p-T diagram, while the proper " liquid " state occupies only a very small proportion of it, and is of very subordinate significance for systems in which high pressures prevail, though, of course, of importance in systems with small pressures, as, *e.g.*, on the earth's surface (Fig. 1).

Furthermore new interest is given to the old question of the existence of a critical point crystalline-fluid,[14] since the two first-mentioned extrapolations, where this question would not have arisen, have now been excluded. In my opinion one cannot give reasons *a priori* (or at any rate those given do not seem to me conclusive) as to whether such a point exists, or whether the curve continues indefinitely; *i.e.*, whether or not there will be continuity of the crystalline and fluid state as in the case of the transition liquid-gas. This does not mean that at temperatures above the hypothetical critical temperature and with very high pressures the substance will be in a non-crystalline state,[15] but only that when expanding the substance isothermally at this temperature it would pass without discontinuity into states to be described as fluid. In the same way the molecular arrangement of a fluid above its normal critical temperature will at high pressures be indistinguishable from that of a liquid, the only difference being that the

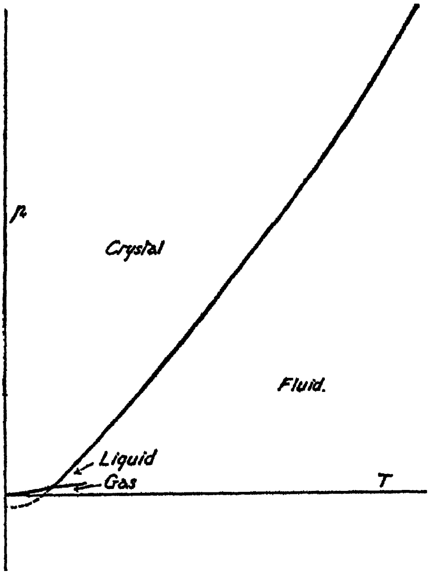

FIG. 1.

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[12] In all these cases formula (1) gave a very good representation of the experimental data, and the same is true of many more experiments that have been done since by other investigators. I mention especially the paper of Clusius and Bartholomé (*Z. physik. Chem., B*, 1935, **30**, 255) in which the melting curves of hydrogen and deuterium are compared, and which proves that the idea of connecting the internal pressure with the melting curve was correct.

[13] Obviously the "practical" applications lie on the astrophysical side; R. Wildt (*Nachr. d. Ges. Wiss., Gottingen*, 1934, **1**, 67) derives from our results that very probably the planets Jupiter and Saturn consist mainly of solid hydrogen at about room temperature.

[14] See, *e.g.*, Kamerlingh, Onnes and Keesom, *Encyclo. Math. Wissensch.*, 1911, **5** (1), 875 ff.

[15] I mentioned this especially in connection with a remark made by Bridgman, *Rev. Mod. Physics*, (1935, **7** (1), 14).

fluid can no longer form a free surface, and in expanding will change continuously to a gaseous form.

What can we now conclude as to the existence of such a critical point. Firstly, if it exists at all, it will certainly lie at relatively very high temperatures; the gap between the fluid and crystalline phases undoubtedly extends over a much higher temperature range than the gap between liquid and gas. Furthermore, if, along the melting curve, either energy or volume becomes equal for both phases the other has to become equal simultaneously. This follows from the Clausius-Clapeyron equation:

$$\frac{\mathrm{d} \ln p}{\mathrm{d} \ln T} = \frac{\rho}{p\Delta V} = \frac{\Delta U}{p\Delta V} + 1 \quad . \quad . \quad . \quad (3)$$

and from the fact that d ln p/d ln T remains finite according to (1). Both properties becoming identical simultaneously is equivalent to the existence of a critical point. Thus if ρ or $p\Delta V$ is measured and either is found to have a tendency to vanish, it would indicate the approach of a critical point.

It has not so far been possible, however, to continue such experiments to sufficiently high temperatures,[16] so that from the discussion of the parameters of the melting curve alone no further conclusions can be drawn besides those already mentioned. It may, however, be possible to find some more indications by considering, in addition, the properties of the single phases themselves. Though less direct, it seems worth while to try this way, as the question of the critical point crystalline-fluid has recently led to many speculations. At least these considerations will supply us with some material for future theories.

Firstly, does experiment support or deny the possibility of finding an equation of state to cover both phases, in which the transition region appears simply as a region of instability, as in the van der Waals' equation. It has often been held that such an equation exists,[14] and recently Frenkel [17] has favoured this view. Should there be an equation of this kind, it would not necessarily imply the existence of a critical point, as one can imagine sets of isothermals given by it which, at any temperature, would show a division into two phases. But apart from the intrinsic interest of this question, a negative result would rule out the existence of a critical point, at least as we understand it at present.

The amount of information at our disposal is small, since the equations of state of both phases have not been investigated in the region in question. We have, however, some indications as to the general behaviour of the energy as a function of the volume, according to which we see a very marked difference between the change of the energy with the volume along one isothermal in the cases of the transitions liquid-gas and crystalline-fluid.

In the first case one finds that with constant temperature the internal pressure $\left(\frac{\partial u}{\partial V}\right)_T$ increases continuously with decreasing volume; this is evident from van der Waals' equation, according to which $\left(\frac{\partial u}{\partial V}\right)_T$ (which we will call π), is equal to $\frac{a}{V^2}$, thus increasing continuously with decreasing volume, also in the unstable region of the transition. Therefore the value for the transition $\frac{\Delta u}{\Delta V}$ (which we will call π^t, and which represents the mean value for $\left(\frac{\partial u}{\partial V}\right)_T$ in the transition region), always lies between the limiting values of the single phases. This remains true also for the real cases and we see in Fig. 2 the data for hydrogen, the π's being calculated as $T\left(\frac{\partial p}{\partial T}\right)_v - p$.

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[16] F. Simon and F. Steckel, *Z. physik. Chem.*, 1931, *Bodenstein-Bd*, 737.

[17] J. Frenkel, *Acta Physico Chimica*, 1935, 3, 633 and 913.

For the transition crystalline-fluid, things are quite different. With very small volumes, such as exist along the melting curve at high pressures, the π's for the single phases become negative on account of the prevalence of the repulsive forces.[18] Thus in the volume region in question the energy of the fluid increases when the volume is reduced, on account of the work done against the repulsive forces. During the transition, however, the energy decreases when passing from the larger fluid volume to the smaller crystal volume, work being done by attractive forces. Continuing the reduction of volume by compressing the solid phase, one has again to do work against the repulsive forces. We can give quantitative data from (1) for π^t, the mean (internal) pressure due to the attractive forces during the transition :

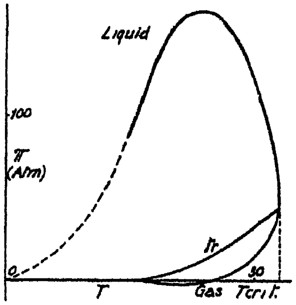

FIG. 2.—Internal pressures for hydrogen along the equilibrium line liquid-gas.

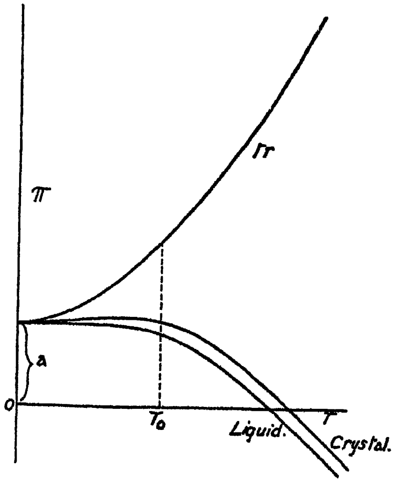

FIG. 3.—Sketch of internal pressures along the melting curve.

$$\pi^t = ca + (c - 1)p \quad . \quad . \quad . \quad . \quad (4)$$

i.e., that at absolute zero (where $p = -a$), $\pi^t = a$, and that it is a linear function of the pressure only,[19] always increasing with rising pressure. Fig. 3 indicates the slope of the π's under equilibrium conditions as a function of T. Both π's for the single phases start at the same value[20] a as π^t and do not change much until reaching temperatures well above the normal melting-point. They then tend towards negative values, while according to (4) π^t slopes immediately upwards, always increasing its distance from π_{crystal} and π_{fluid}.

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[18] See, *e.g.*, Eucken, *Lehrbuch der Chem. Physik*, 1930, p. 193 ff.

[19] With the help of Mr. Stanger I have compared this consequence of (1) with all the experimental data given by Bridgman, and in the great majority of cases π^t plotted against p gives very nearly a straight line. In the few cases where there are small deviations it was not possible to improve the agreement by adding a T function, as van Laar thought essential (*Kon. Akad. v. Wetenschappen*, 1934 **35**, 624).

This very different behaviour may suggest at first sight an essential difference between the two transitions, making it impossible in principle to construct an equation of state to cover the crystalline and fluid ranges simultaneously, but an analysis of the isothermals in the p-V diagram shows that this is not so. This question is essentially connected with the behaviour of the volumes along the equilibrium curve. The volume of the phase with the smaller density decreases for both transitions with rising equilibrium pressure. In the case of the transition liquid-gas, the volume of the liquid increases, and both volume curves join, in the well-known way, at the critical temperature. Under these conditions the value of π^t must lie between those of the single phases if we are to construct an equation of state covering both phases.

On the contrary π^t will have to possess values larger than both π's of the single phases if the volume of the denser phase decreases also with rising equilibrium pressure. This is, in fact, what one observes along the melting curve, the volume of the crystal decreases with rising melting pressure,[21] in all known normal cases. This is evident also from the behaviour sketched in Fig. 3. π^t being larger than the single π's means that at a certain equilibrium pressure dp/dT is larger than the $\left(\frac{\partial p}{\partial T}\right)_v$ of the single phases, and this is, of course, equivalent to a decrease of the volumes with rising temperature along the melting curve.

Thus this different behaviour of the energy is, in fact, a necessary consequence of the different behaviour of the volumes, and so, from the thermodynamical point of view, evidence cannot be given for or against the existence of an equation of state covering both phases. I may mention here, however, one other point, which seems to favour the existence of such an equation, namely the fact that a (which is responsible for the melting curve) is also connected with the transition to the gaseous state.[22]

Further let us see whether or not the properties of the two phases approach along the melting curve, and for this purpose let us consider the change of the entropy of the separate phases along it. The entropy, being a measure of the state of disorder in a substance, is an appropriate quantity to survey in order to find out whether or not the two substances become identical. From Bridgman's work it is known that the heat of fusion remains constant to a first approximation, at least in the region investigated so far. The entropy difference will therefore decrease with rising melting temperature. This fact, however, does not tell us enough, since the entropy of the solid may perhaps decrease with rising melting temperature, *i.e.*, the effect of the pressure tending to diminish the entropy will be greater than the effect of temperature tending to increase it. In that case a diminishing entropy difference could nevertheless become larger with rising temperature, compared with the entropy of the solid, and it would be difficult to draw any conclusions.

[20] This is a trivial consequence of dp/dT remaining finite at absolute zero.

[21] And therefore *a fortiori* also the volume of the fluid phases, as ΔV decreases rapidly.

[22] To a first approximation $a \, . \, v$ gives the heat of evaporation.

For a few cases the necessary data [23] exist for calculating the entropy of the solid along the melting curve, and, in connection with the heats of fusion, the entropy of the liquid is also given. In Fig. 4 these data are given for potassium, for which the best foundations exist, and we see that as the entropy of the solid increases that of the liquid diminishes. Sodium and argon show analogous behaviour.

The rising of the curve for the solid phase [24] means that the influence of temperature prevails over that of pressure, and the disorder of this phase increases, in other words the temperature of the substance measured relatively to a characteristic pressure (*e.g.*, the Debye θ) still rises. In the liquid, however, the opposite happens, increasing pressure forcing the liquid, in spite of the rising temperature, into an ever higher state of order. Therefore, from the viewpoint of the state of order, the phases become more and more alike with rising melting temperature.

Fig. 5 shows diagrammatically the behaviour of the entropy for the three states of aggregation under equilibrium conditions. It is difficult to predict what will happen to the lines for the transition crystal-fluid at higher temperatures. If there is a critical point [25] similar to the normal one, then the entropy and the volume curves should join in the same way as those for the transition liquid-gas. It is not easy, however, to see how the volume curves can join in this way as $\left(\frac{\partial p}{\partial T}\right)_v$ for the solid would then have to become larger than dp/dT near the hypothetical critical point, and the equation of state for the solid does not give any indication that this should be expected. If there is no such point they would continue and probably approach each other asymptotically. The possibility

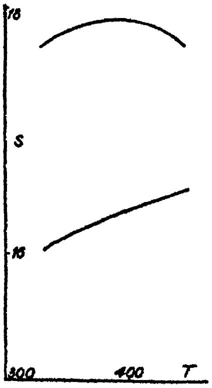

FIG. 4.—Entropy of solid and liquid potassium along the melting curve.

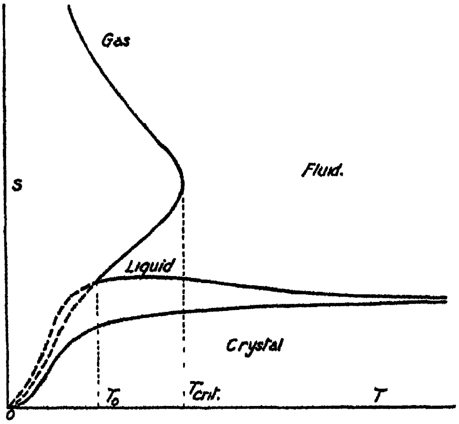

FIG. 5.—Sketch of entropy along equilibrium curves for all states of aggregation.

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[23] There is a certain margin in these calculations, but it is not so great that the character of the curves would be changed. Details of the calculations will be published later.

[24] If this result were general, one could never melt a crystal by adiabatic compression, a result that seems to be of interest for astrophysical problems.

[25] Recently Frenkel [17] suggested that there must be a critical point at the lower end of this curve. I cannot see, however, from the evidence of the experimental data, any indication that the differences of energy and volume should vanish at low temperatures.

that they might meet in a cusp, must, however, not be excluded, though such a critical point would be of a quite different type. It is also possible that the region where these phenomena are to be expected lies at such high temperatures that we are no longer concerned with normal atoms and then the whole question would be of a different character.

Only by experiment can further conclusions be reached, and it is obvious that low boiling substances should serve as models. Dr. Michels and I hope very soon to continue experiments of this kind in his laboratory in Amsterdam.

Summary.

The range of stability of the fluid state is discussed with special reference to the continuation of the melting curve to high temperatures. It is pointed out that up to the present the experimental data do not give any indication that would exclude the existence of a continuity between the crystalline and the fluid state. In particular it is shown that along the melting curve the entropy of the solid and liquid phases approach an intermediate value, which indicates a growing similarity between the phases with rising melting temperature.

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A PARTITION FUNCTION FOR LIQUIDS.

By Roy F. Newton and Henry Eyring.

Received 11*th August*, 1936.

The method of approach adopted here is to calculate the vapour pressure of liquids from a knowledge of their heat capacities, heats of vaporisation, and coefficients of expansion. This requires a more detailed picture than thermodynamics provides, but stops short of the general statistical theory which would provide for the calculation of these latter properties also, using only a potential energy function for the molecular system.

We adopt the following form for the partition function of the ideal liquid and its vapour respectively:

$$F_l = \frac{(2\pi mkT)^{3/2}}{h^3} V_f \,.\, R_l \,.\, Vib_l \quad . \quad . \quad . \quad (1)$$

$$F_g = \frac{(2\pi mkT)^{3/2}}{h^3} V_g \,.\, R_g \,.\, Vib_g \exp.\left(-\frac{E_0}{kT}\right) \quad . \quad . \quad (2)$$

in which R_l and R_g are the rotational partition functions, and Vib_l and Vib_g are the vibrational partition functions, respectively, for the liquid and gas. We shall call V_f the "free volume." At constant pressure it will depend on the temperature, and we will assume that it can be expressed by an equation of the form

$$V_f = BT^n \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We now substitute (3) in (1) and use the fact that the heat capacity at constant pressure is

$$C_{p(l)} = \frac{d}{dT}\left(RT^2 \frac{d \log F_l}{dT}\right) + \left(\frac{d(pV_l)}{dT}\right)_p \quad . \quad . \quad (4)$$

At temperatures not too near the critical point the last term of (4) is negligible. Obtaining C_v of the gas in an analogous manner from equation (2), but using the restriction of constant volume, we find

$$C_{p(l)} = C_{v(g)} + Rn \quad . \quad . \quad . \quad . \quad (5)$$

when the rotational and vibrational terms of (1) are equal to those of (2). Substituting (5) in (3) we now obtain

$$V_f = BT^{(C_{p(l)} - C_{v(g)})/R} \quad . \quad . \quad . \quad . \quad (6)$$

To evaluate B we assume that $V_f^{1/3}$ represents the linear freedom of the molecular centre, and that the coefficient of linear expansion is

$$\frac{\mathrm{d}V_f^{1/3}}{V_l^{1/3}\mathrm{d}T} = \frac{\alpha}{3} \quad . \quad . \quad . \quad . \quad (7)$$

in which α is the coefficient of cubical expansion. This then gives

$$V_f = \left(\frac{RT\alpha}{C_{p(l)} - C_{v(g)}}\right)^3 V_l \quad . \quad . \quad . \quad (8)$$

so that (1) becomes

$$F_l = \frac{(2\pi mkT)^{3/2}}{h^3}\left(\frac{RT\alpha}{C_{p(l)} - C_{v(g)}}\right)^3 V_l \, . \, R_l Vib_l \quad . \quad . \quad (9)$$

For equilibrium between the liquid and vapour $F_l = F_g$, and since $V_g = kT/p$, we immediately obtain for the vapour pressure

$$p = \frac{kT}{V_l}\left(\frac{C_{p(l)} - C_{v(g)}}{RT\alpha}\right)^3 \exp. (-E_0/kT) \quad . \quad . \quad (10)$$

if the partition functions for rotation and vibration of the liquid and gas are equal. If we wish to express (10) in terms of the ordinary heat of vaporisation, since

$$\Delta H = E_0 + \int_0^T (C_{p(g)} - C_{p(l)})\mathrm{d}T\,^*$$

we obtain

$$p = \frac{kT}{V_l}\left(\frac{C_{p(l)} - C_{v(g)}}{RT\alpha}\right)^3 \exp. \left(\frac{\int_0^T (C_{p(g)} - C_{p(l)})\mathrm{d}T}{RT}\right)$$
$$\exp. (-\Delta H/RT) \quad (11)$$

Since sufficiently reliable data on the heat capacities of liquids and their vapours at low temperatures are unfortunately not available for testing equation (11), we will estimate the value of

$$\frac{1}{RT}\int_0^T (C_{p(g)} - C_{p(l)})\mathrm{d}T$$

by substituting in (11) the known values of the vapour pressures, heat capacities and coefficients of expansion at ordinary temperatures, With the notable exception of mercury, the calculated values appear plausible, since the heat capacities of the liquids certainly decrease markedly with decreasing temperatures. Some of the liquids given probably do not exhibit free rotation, in which case (11) is not strictly applicable.

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* In this equation E_0 is evidently the energy per mole, not per molecule as in (10). To avoid complicating the notation, we will use the same symbols for molal and molecular quantities, since the use of k or R always suffices to indicate which quantity is intended.

On calculating $C_{v(l)}$ from equation (1), assuming that V_f is constant when V_l is constant, we find that

$$C_{v(l)} = C_{v(g)} \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

if the rotational and vibrational terms are equal for liquid and gas. C_v of the liquid is very nearly equal to C_v of the gas, as is shown in Table I. At constant pressure, however, the heat capacity of liquids are conspicuously high as compared to those for the gaseous state. This has recently been commented upon by MacLeod.[1]

The data for water are for 100° C. and those for mercury are for 0° C. That for the other substances is for room temperature. The data have been compiled in part from Landolt-Börnstein, from the International Critical Tables, and from the table of MacLeod.[1]

Equation (12) constitutes a test of the applicability of (11) to a substance. When (12) is true, we can use the thermodynamic equation $C_{p(l)} - C_{v(l)} = \alpha^2 V_l T/\beta$ to rewrite (11) in the form

$$p = \frac{RT}{V_l}\left(\frac{\alpha V_l}{R\beta}\right)^3 \exp.\left(\frac{\int_0^T (C_{p(g)} - C_{p(l)})\mathrm{d}T}{RT}\right) \exp.\left(\frac{-\Delta H}{RT}\right) \qquad (13)$$

TABLE I.

	$C_{p(l)}$.	$C_{v(g)}$.	$C_{p(l)} - C_{v(g)}$.	V_l.	$\alpha \times 10^3$.	$C_{v(l)} - C_{v(g)}$.	ΔH.	p.	$\frac{1}{RT}\int_0^T (C_{p(l)} - C_{p(g)})\mathrm{d}T$ Calc.
Br_2 . . .	17·1	6·8	10·3	54·6	1·114	2·5	6980	173	3·88
CS_2 . . .	18·3	10·0	8·3	60·3	1·218	1·7	6400	298	3·32
Acetone . .	29·8	19·9	9·9	73·3	1·487	− 0·45	7230	185	2·10
Ethyl acetate .	42·1	30·0	12·1	97·7	1·389	− 0·75	8550	72·8	1·29
Ethylene chloride	30·2	21·0	9·2	78·7	1·161	− 0·4	8440	61·0	1·58
Ethyl bromide .	23·6	14·1	9·5	76·2	1·418	0·3	6530	386	2·55
Benzene . .	32·0	21·0	11·0	88·8	1·24	0·9	7530	74·8	3·37
$CHCl_3$ . .	27·9	17·0	10·9	79·7	1·273	− 2·2	7040	160	3·25
CCl_4 . .	30·9	20·0	10·9	105·1	1·228	0·6	7740	91	3·47
Ethyl ether .	40·0	31·0	9·0	103·8	1·584	− 1·5	6215	442	4·45
Water . .	18·0	6·5	11·5	18·8	0·75	9·5	9720	760	3·37
Mercury . .	6·57	2·98	3·59	14·72	0·182	2·8	13600	0·000185	8·28

From Table I. it is evident that (12) holds approximately for many substances. If the divergence from this equality of heat capacities arises only from the fact that R and Vib are different for the liquid and gas, we may expect the following equations to hold :

$$p = \frac{RT}{V_l}\left(\frac{\alpha V_l}{R\beta}\right)^3 \frac{R_g}{R_l}\frac{Vib_g}{Vib_l} \exp.\left(\frac{\int_0^T (C_{p(g)} - C_{p(l)})\mathrm{d}T}{RT}\right) \exp.\left(-\frac{\Delta H}{RT}\right) \qquad (14)$$

or

$$p = \frac{RT}{V_l}\left(\frac{C_{p(l)} - C_{v(l)}}{RT\alpha}\right)^3 \frac{R_g}{R_l}\frac{Vib_g}{Vib_l}$$

$$\exp.\left(\frac{\int_0^T (C_{p(g)} - C_{p(l)})\mathrm{d}T}{RT}\right) \exp.\left(-\frac{\Delta H}{RT}\right) \qquad (15)$$

Finally we may expect cases in which the vapour pressure is best expressed by the equation

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[1] D. B. MacLeod, *Trans Faraday Soc.*, 1935, **31**, 746.

$$p = \frac{RT}{V_l}\left(\frac{C_{p(l)} - C_{v(g)}}{RT}\right)^3_{\text{ideal}} \cdot \frac{R_g}{R_l}\frac{Vib_g}{Vib_l}$$
$$\text{exp.}\left(\frac{\int_0^T (C_{p(g)} - C_{p(l)})\mathrm{d}T}{RT}\right)\text{exp.}\left(-\frac{\Delta H}{RT}\right) \quad (16)$$

in which the quantity with the subscript "ideal" is to be taken equal to the value for ideal substances. Unfortunately, the data at present available make a systematic quantitative test of the proposed relations difficult. Many of the rules for the boiling-points of organic liquids, however, are readily interpreted using (16) if R_l is assumed to correspond to oscillations instead of rotations. This leads to values of R_g/R_l greater than 1, and to the generalisation that, other things equal, greater moments of inertia for one of two similar large organic molecules gives a correspondingly greater value for the quantity R_g/R_l. This is of importance for large molecules which differ only by one or more isotopic atoms. The fact that heavy benzene has a higher vapour pressure than ordinary benzene can be explained in this way.[2]

The same effect is present in the cases of light and heavy water and ammonia, but the effect on the vapour pressure is over-shadowed by the change in heat of vaporisation due to the differences in zero-point energies.[3] The rule that moving a heavy substituent toward the end of a long chain lowers the boiling-point also exemplifies the same proposition.

Instead of assuming a free volume V_f we can assume a potential function for the liquid molecule of the form

$$V = a(|\,x\,|^s + |\,y\,|^s + |\,z\,|^s).$$

This leads to the partition function.

$$F_l = \left(\frac{(2\pi mkT)^{3/2}}{h^3}\right)\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\text{exp.}$$
$$-\frac{a}{kT}(|\,x\,|^s + |\,y\,|^s + |\,z\,|^s)\mathrm{d}x\mathrm{d}y\mathrm{d}x \,.\, R_l \,.\, Vib_l \quad (17)$$

We may now write

$$I^3 = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\text{exp.}\left(-\frac{a}{kT}\right)(|\,x\,|^s + |\,y\,|^s + |\,z\,|^s)\mathrm{d}x\mathrm{d}y\mathrm{d}z$$
$$= \left[2\int_0^{\infty}\text{exp.}\left(-\frac{ax^s}{kT}\right)\mathrm{d}x\right]^3.$$

Solving, we obtain

$$I = \frac{2}{s}\Gamma\left(\frac{1}{s}\right) \cdot \left(\frac{kT}{a}\right)^{1/s} \quad . \quad . \quad . \quad (18)$$

Substituting this value in (17) and calculating the heat capacity as before we obtain

$$\frac{C_{p(l)} - C_{v(g)}}{3R} = 1/s \quad . \quad . \quad . \quad . \quad . \quad (19)$$

To evaluate a we calculate the average displacement of the molecule

$$\bar{x} = \frac{\int_0^{\infty} x\,\text{exp.}\left(-\frac{ax^s}{kT}\right)\mathrm{d}x}{\int_0^{\infty}\text{exp.}\left(-\frac{ax^s}{kT}\right)\mathrm{d}x} = (kT/a)^{1/s}\frac{\Gamma\left(\frac{2}{s}\right)}{\Gamma\left(\frac{1}{s}\right)}.$$

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[2] Bowman, Benedict, Kirkpatrick and Taylor, *forthcoming publication.*

[3] Topley and Eyring, *J. Chem. Physics*, 1934, **2**, 217.

As before we write the coefficient of linear expansion

$$\frac{\alpha}{3} = \frac{2}{V_l^{1/3}}\frac{d\bar{x}}{dT} = \frac{2\left(\frac{kT}{a}\right)^{1/s}\Gamma\left(\frac{2}{s}\right)}{V_l^{1/3}sT\,\Gamma\left(\frac{1}{s}\right)} \quad . \quad . \quad . \quad (20)$$

Using (19) and (20) and the value for I we can rewrite (17)

$$F = \frac{(2\pi mkT)^{3/2}}{h^3}\frac{\alpha^3T^3V_l}{27}\left(\Gamma\left(\frac{C_{p(l)} - C_{v(g)}}{3R}\right)\right)^6 \left(\Gamma\left(\frac{2(C_{p(l)} - C_{v(g)})}{3R}\right)\right)^{-3} . R_lVib_l \quad (21)$$

For $C_{p(l)} - C_{v(g)} = 6$, equation (21) becomes identical with (9). For smaller values of this quantity, (21) is larger than (9), and for larger values it is smaller. Equation (9) seems to agree considerably better with the rather meagre experimental material. This might be expected from the nature of the field in which a molecule moves. If we think of a molecule occupying a small volume with its neighbours at their average positions and acted upon by an exponential repulsion varying rapidly with the distance, and an attractive potential varying inversely as the sixth power of the distance, we find that the molecule has its lowest potential around the edges of this volume with only slightly higher potentials at the centre, and the edges of the volume are bordered by a rapidly rising potential due to the repulsive field. Thus in effect a molecule is restricted to motion in a nearly force-free box from which it only occasionally escapes, and it is not surprising that the free volume concept embodied in (9) accounts for the facts better than that of a potential restraining the molecule to a mid-position embodied in (21). Furthermore, at temperatures for which the molecules of the liquid exhibit free rotation, the free volume concept leads immediately to the relation $C_{v(l)} = C_{v(g)}$, since we then have the well-known problem of the motion of a molecule in a box for the translational part of the partition function. If rotation is much restricted in the liquid, this relation fails, even though the free volume concept may still be applicable.

We do not expect these relations to hold near the critical point, for in addition to the fact that the external work term of (4) is then no longer negligible, the increasing concentration of holes in the liquid[4] makes the coefficient of expansion abnormally large, and also seriously affects other relevant properties.

It may be of interest to note that for a substance obeying van der Waals' equation, $\alpha/\beta = R/(V - b)$, and (13) can be transformed to $p = \frac{kT}{V_l}\left(\frac{V_l}{V_l - b}\right)^3 \exp.(-E_0/kT)$, which, for large V_l reduces to the gas law since

$$\frac{V_l}{V_l - b} \doteq 1 \quad \text{and} \quad e^{-E_0/kT} \doteq 1.$$

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[4] Eyring, *J. Chem. Physics*, 1936, 4, 283.

Summary.

A partition function for liquids is given involving the coefficient of expansion and the specific heats. The equation leads to reasonable results for vapour pressures of most of the liquids examined.

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*GENERAL DISCUSSION.**

Professor J. A. Prins (*Wageningen*) said: Dr. Frenkel says that the "structure diffusion coefficient" is a function of temperature not yet studied quantitatively. The following expression for this quantity is, however, given:[5]

$$\Delta = \frac{\overline{\xi^2}}{6\tau} = \frac{KkT}{6a^2},$$

where K is the compressibility, a the molecular diameter of the liquid. As remarked in Bernal's paper, this simple expression is only valid if the co-ordination in the liquid does not depend markedly on temperature; it is, however, a good approximation in many cases and certainly sufficiently so for the approximative argument of Professor Frenkel's paper.

Dr. M. Magat (*Paris*) said: It seems worthy of note, although we do not yet know its real significance, that as we can see from the potential curve of the solid at absolute zero temperature, *for a given inner energy, the volume of the liquid is smaller than would be that of the solid, if it could exist.*

Dr. W. R. van Wijk (*Amsterdam*) said: The application of the theory of diffusion to the calculation of the viscosity of liquids in equations (1), (2) and (3) requires further explanation. The equation $\delta^2 = Dt$ only holds when the time t is so long that the diffusing particle has undergone a very large number of collisions during the displacement δ, so that the particle has covered an extremely irregular zig-zag route. The "Diffusion relation" does not apply to a short-time displacement, in which only few collisions occur; for very short times, in which the velocity of the moving particle may be considered to be constant, the displacement must, of course, increase linearly with the time.

The relation between δ and t for all times has been calculated by L. S. Ornstein[6] for the Brownian movement of a free particle with a mass which is very large in respect of the mass of the molecules of the surrounding medium.

The use of the self-diffusion coefficient to calculate a displacement in a time of order of the time between two switches therefore decidedly requires a further justification.

Dr. J. A. V. Butler (*Edinburgh*) said: Dr. W. J. C. Orr and I[7] have measured the coefficient of diffusion of deuterium hydroxide in water, which may be expected to be practically the same as that of the self-diffusion of water. The value obtained indicated that the molecule escaped from its "territory" once in about 1000 vibrations at 15°. Introducing this figure into

$$\tau/\tau_0 = e^{U/RT},$$

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* On three preceding papers.

[5] J. A. Prins and H. Petersen, *Physica*, 1936, **3**, 147.

[6] A survey of the older calculations is given in G. E. Uhlenbeck and L. S. Ornstein, *Physical Review*, 1930, **36**, 323.

[7] *J. Chem. Soc.*, 1935, 1273.

we obtain $U = 4000$ cals., while from the temperature coefficient of the diffusion coefficient the activation energy of the diffusion process was found to be about 5000 cals. The simple picture of the diffusion process, in which the fraction of the oscillations leading to a " switch " is determined by the excess energy required, is thus reasonably adequate in this case. It may be observed that the temperature coefficient of the diffusion was found to be not identical with that of the viscosity, but water is a very abnormal liquid and better agreement might be found with structureless liquids.

Professor J. H. Hildebrand (*Berkeley, Cal.*) said : It is remarkable that the equations of state of fluids and solids, which are likely to be very complicated, should combine to yield such a simple equation for the equilibrium between them. It suggests that the phenomenon of melting is a comparatively simple one, involving much the same sort of entropy change in all cases, just as in vaporisation. If the formula is differentiated with respect to temperature we find, by the aid of a well-known thermodynamic relation, that the change of entropy *per se* in melting is proportional to a power of the absolute temperature. Professor Simon's equation will serve as an important check on equations of state.

Mr. J. D. Bernal (*Cambridge*) said : From the experimental as well as the theoretical standpoint the discussion of the continuity of the liquid and crystalline states still remains a matter of extrapolation. It is clear from Professor Simon's own measurements that the entropies of the two states approach at high temperatures. There is no evidence to indicate that the curves turn over and run into one another and, as yet, little evidence that they do not move asymptotically towards either one common entropy or two entropies at a finite distance apart. I am inclined to favour the latter hypothesis because according to my views there should be especially for close-packed substances—and at high temperatures all solids are close-packed—there should exist a region of unrealisable configuration between that of the most irregular solid and the most regular liquid. I have not, however, been able to prove that this is the case, and I am still prepared to accept the idea that at sufficiently high temperatures the motions of the atoms may be such as cannot be described on a comparatively static model with which I have worked.

The whole question, however, may be an academic one because for all ordinary atoms the pressures and temperatures required to bring about an approximation of crystal to liquid may be such as to cause the breakdown of the outer electronic shells of the atoms with a consequent transition to a totally different melting curve. It would be very useful to push further into this largely unknown territory because, although such conditions are not likely to be realised in the laboratory, they have an important bearing on the state of matter in the interior of the earth and in stars. We would like to know, for instance, whether in these conditions matter exists in a crystalline or liquid form, or in a strictly intermediate state.

While I am in general agreement with the first part of Professor Frenkel's paper, which treats viscosity as a form of re-arrangement of equilibrium positions of atoms and liquids, I cannot agree with the second part of the paper. I had at one time thought that the continuity between liquids and solids might, as he has suggested, be achieved, not at increased pressures, but at negative pressures. I am convinced now that this continuity could not theoretically exist and that even if it could it would be for two separate reasons impossible to realise it physically. According to the theory set out in my paper the characteristic difference between crystals and liquids is the degree of disorder which I consider in general is incapable of having any values between a maximum degree of disorder for a crystal and a minimum value for a liquid. This minimum itself will depend on the pressure. At low pressures and particularly at negative pressures the degree of disorder must increase and consequently the expanded state there would be more and not less difference between a crystal and a liquid. In particular the difference of volume at the melting-point will increase with diminished pressure. The physical state of a crystal subjected to very large negative pressures, supposing this could be done without secondary effects such as cracking, would be to lead to a state of affairs of complete fragmentation where certain groups of atoms would come together at small distances and be separated from other groups by relatively large distances. Such a configuration would for large degrees of expansion have lower energy than one where the atoms were approximately equidistant from one another. But there is a second reason why Professor Frenkel's view is physically unrealisable. He postulates the continuous transformation as one occurring at low temperatures. At these temperatures however, not only the liquids but the crystals would be in a state where in relation to change of configuration no thermo-dynamic equilibrium is possible. Any continuous change of the nature suggested by Professor Frenkel would be one which demanded full freedom to assume configurations of minimum free energy, and thus this transformation is excluded under the only conditions for which he considers it possible.

Professor F. Simon (*Oxford*), in reply, said: Concerning Frenkel's stipulation that there should be a critical point terminating the melting curve at low temperatures, I have already remarked[8] that I cannot see any experimental indication of its existence. I should perhaps add here that the case of helium is definitely against it. In this case we can extrapolate with certainty to absolute zero, and we find two different phases which show absolutely different volumes and energies, so that there is no question at all of both phases becoming identical.

Mr. Bernal asked why in Fig. 5, which indicates the probable slope of the entropy along the equilibrium curves, the lines for the transition crystalline-fluid have been extended so far. The reason is that although the data for the actual entropy calculations do not extend to relatively very high temperatures, we know, from the experiments with the model substances, that a discontinuous change from crystal to fluid still exists at relatively very much higher temperatures.

Professor H. Eyring (*Princeton*), in reply, said: Recent work by Eyring and Hirschfelder[9] proceeding further along the general lines followed by Newton and Eyring makes it possible to state some of the points in the above paper more precisely.

Use of the concept of a free volume, in which each molecule is free to move, leads to a relationship of the type:

$$V_f = b^3(V_l^{\frac{1}{3}} - d)^3 \quad . \quad . \quad . \quad . \quad (22)$$

so long as V_f is small. Here d is the diameter from which each molecule excludes neighbours and b is a factor which has to do with the type of packing. In the simple case of molecules arranged at the corners of cubes b is 2, provided that each molecule is free to move in the space to which it would be restricted were its neighbours fixed at their mean position. This idea of a free volume, then, leads to the equation,

$$p_{\text{vap.}} = n^3RTb^{-3}V_l^{-1}\left(\frac{\Delta H}{RT} - 1\right)^3 \exp.\left(-\frac{\Delta H}{RT}\right) \quad . \quad . \quad (23)$$

where n is defined by saying that the potential energy of the liquid is $\Delta H - RT = \frac{a}{V_l^n}$. Hildebrand's investigations show that for most normal liquids $n = 1$ and, if b^3 be taken equal to 8, we have a vapour pressure equation which gives the Trouton and Hildebrand rules with constants which agree with experiment. Equation (23) is, of course, the analogue of (10) above. The theory leads to an equation of state for the liquid of the van der Waals' type, from which coefficients of thermal expansion and compressibility are derived in satisfactory agreement with experiment.

[8] *This vol.*, p 65.

[9] *J. Physic. Chem.*, in press.

REDUCED TEMPERATURE AND GENERAL PROPERTIES OF PURE LIQUIDS.

By E. Bauer, M. Magat and M. Surdin (*Paris*).

Received 19*th September*, 1936.

1. Introduction.

In a comparative and systematic study of the properties of pure liquids and their variation as a function of temperature, it seems natural and convenient to adapt the following expression as "reduced temperature."

$$\theta = \frac{T - T_f}{T_c - T_f} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where T is the Kelvin temperature; T_f the melting-point temperature, or more correctly, the triple-point temperature, and T_c the critical temperature.

This new variable assumes all values between 0 and 1, when the temperature of the liquid passes from T_f to T_c, thus sweeping the whole range of the existence of the liquid, and allows us to place all liquids on the same graph, although the margin $T_c - T_f$ is very different for different liquids (20° for H_2 and 1500° for Hg). At the critical point θ equals the reduced temperature of van der Waals.

In what follows we shall see that the use of this new variable simplifies the study of the static properties of liquids, in the same way as the reduced variables of van der Waals do for gases. It was not yet possible to find a reduced pressure, but this is not of much importance for the present work, because the properties of liquids vary slowly with pressure. For that reason we simply used the figures found in the tables which generally refer to the normal or the vapour pressure (see the discussion relative to volume and compressibility).

2. Molecular Volume.

Fig. 1 represents ratios $\frac{V_T}{V_f}$ (V_T molecular volume at temperature T, V_f at the melting-point) plotted against θ, this is done for seventeen different liquids, those as dissimilar as possible being chosen. Water and H_2 excepted, we are able to trace a mean curve, where the experimental deviations are less than 2 per cent., for θ up to 0·99. At the critical point, where the curve is vertical, the deviations are greater.

The volume was measured under vapour pressure which obviously changes with θ. We have tried to calculate the value for one single pressure, *i.e.*, critical pressure; the resultant correction was within the limit of errors, owing to the low compressibility of liquids at low temperatures, and to the small difference of pressure near $\theta = 1$. For certain liquids, Xe, N_2O, SO_2, CH_3OH, C_3H_7OH, $(CH_3)_2O$, we had no experimental data as to their volume at the melting-point, so we deduced these V_f by assuming the validity of the general law, for one single temperature, an assumption which was justified by the complete concordance for all other temperature.

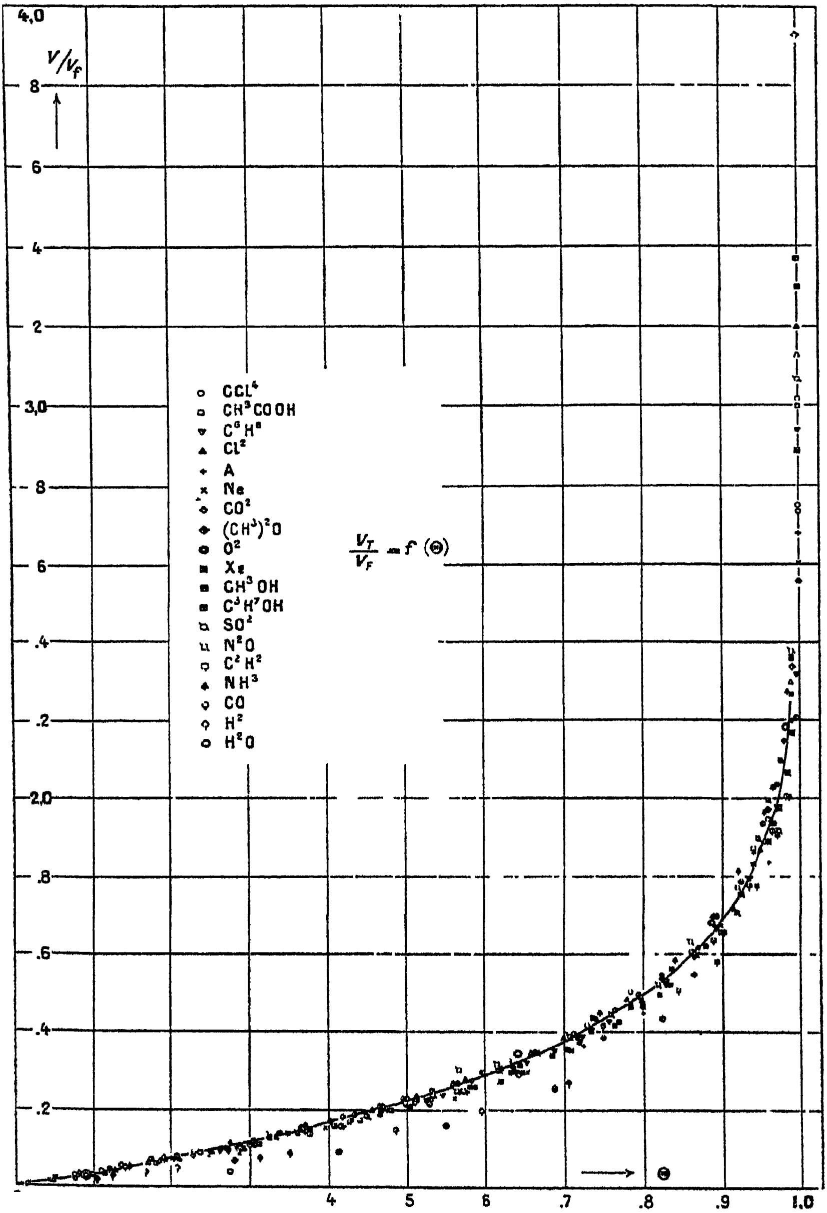

Fig. 1.

H_2 and H_2O follow similar curves but lower than the main one; their volume increases less with temperature than those of other liquids. This seems quite natural: for water, the quasi-tetrahedric structure contains large empty spaces, which can be packed when temperature increases; for H_2 the volume at the melting-point is abnormally large, owing to the "zero-point energy," which is important for such light molecules.

The mean curve may be formulated by an empirical law, containing only two arbitrary constants:

$$V_T/V_f - 1 = 3{\cdot}36[1 - (1 - \theta)^{1/10}] \quad . \quad . \quad . \quad (2)$$

or

$$\log (4{\cdot}36 - V_T/V_f) = \tfrac{1}{10} \log (1 - \theta) + \log 3{\cdot}36 \quad . \quad (2a)$$

The values of V_T/V_f calculated by this formula are represented by the full curve on Fig. 1, and agree well with the mean experimental data.[1] In spite of the great uncertainty for $\theta = 1$, the calculated value $V_T/V_f = 4{\cdot}36$, for this temperature, agrees fairly well with the value 4 given by the law of D. Berthelot, if we suppose roughly the co-volume to be V_f.

TABLE I.

θ.	V/V_f Calc.	V/V_f Obs. Mean.
0	1	1
0·2	1·074	1·074
0·5	1·225	1·220
0·75	1·433	1·425
0·9	1·692	1·692
0·975	2·039	2·040

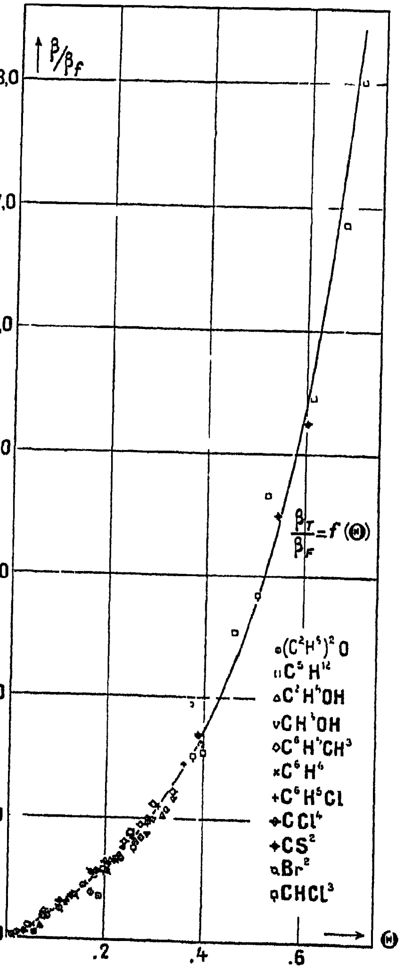

FIG. 2.

3. Compressibility.

Although the experimental data for compressibilities (β) are scarce and less accurate than those of densities, it is possible to establish an analogous graph (Fig. 2), where β_T/β_f are plotted against θ for ten different liquids. The values of β used were those obtained from the experimental data extrapolated to zero pressure. The experiments were all carried out for θ smaller than 0·7 and the vapour pressure for these θ is always small. For those liquids, where β_f was unknown we proceed in the same way as for the volumes. The formula which represents fairly well β_T/β_f as a function of θ, for θ varying from 0 to 0·7 is the following

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[1] For more ample information see E. Bauer, M. Magat and M. Surdin "Contribution à l'étude de l'état liquide," *Journal de Physique*, November, 1936.

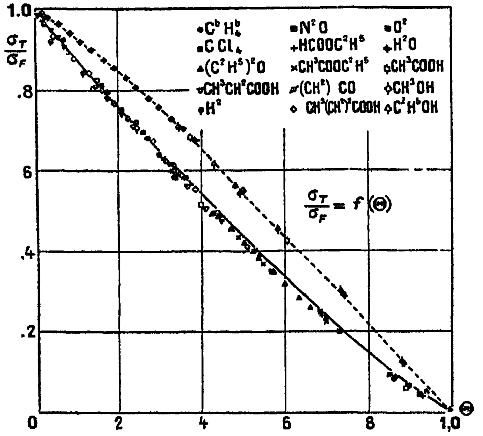

FIG. 3.

$$\frac{\beta_T}{\beta_f} = \frac{1 - \theta^1}{(1 - \theta)^2} \quad . \quad (3)$$

4. Surface Tension.

The Eötvos law concerning the surface tension is

$$\sigma V^{2/3} = K(T_c - T) \quad (4)$$

where σ is the surface tension, V the molecular volume, k a constant which is 2·12 for normal liquids following this law; T_c, in fact, is a little smaller than the critical temperature (4° or 6° less). This law combined with our formula (2) shows that σ_T/σ_f for all normal liquids is an universal function of θ

$$\frac{\sigma_T}{\sigma_f} = \left(\frac{V_T}{V_f}\right)^{2/3}(1 - \theta) \quad . \quad . \quad . \quad . \quad (5)$$

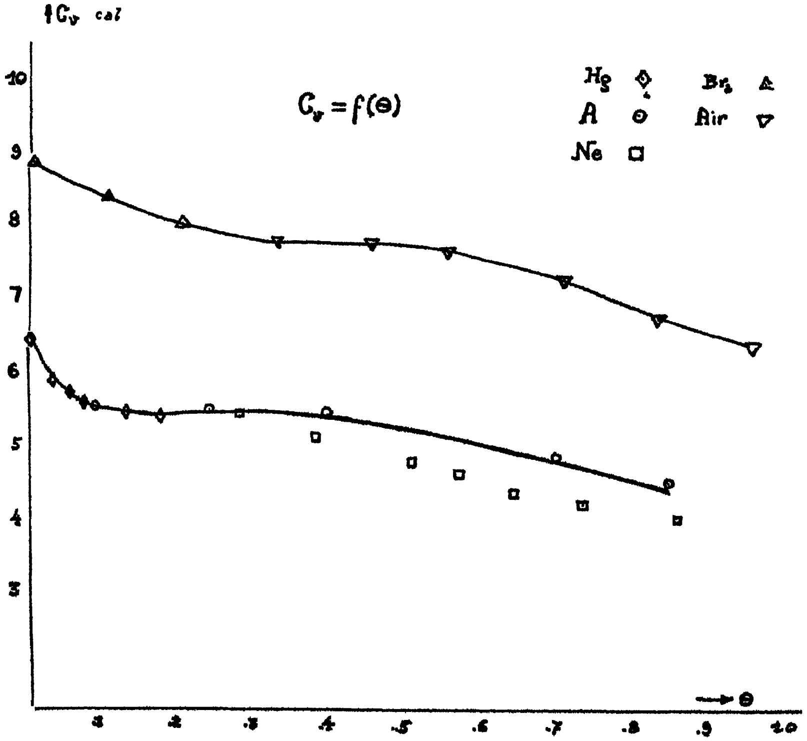

FIG. 4.

This formula agrees fairly well with experimental results (full curve, Fig. 3).

The experimental results for acetone, which does not follow Eotvos' law, are nevertheless represented by the same curve, while all other abnormal liquids: water, HCOOH, CH_3COOH, alcohols, follow another law (dotted curve).

5. Specific Heat.

It is evident that H_2 and He must be put apart in a special class, because of their melting-point being lower than their equipartition temperature, and therefore the quantum phenomenon determines an increase of specific heat in the liquid.

(*a*) Mono-atomic Liquids.

The atomic heats of Ne, A, and Mercury are plotted against θ (Fig. 4). It seems that the points representing C_v for A and Hg form a single curve to which Ne points approach, although we have to take into consideration that the Ne used by Clusius for measurements was not absolutely pure (*cf.* the paper of Bartholomé and Eucken). At the melting-point C_v is somewhat higher than 6 cal., then decreases rapidly, from $\theta = 0{\cdot}1$ to $0{\cdot}35$ seems to keep a fairly constant value, then decreases again and seems to approach 4 calories at the critical point. It is to be noted that L. Brillouin found theoretically that $C_v = 4$ cal. for ideal liquids.[2] Anyhow, the experiments of Eucken and Hauck[3] show that there is no discontinuity in C_v for the critical point, C_v tending progressively to 3 cal. for perfect monoatomic gases.

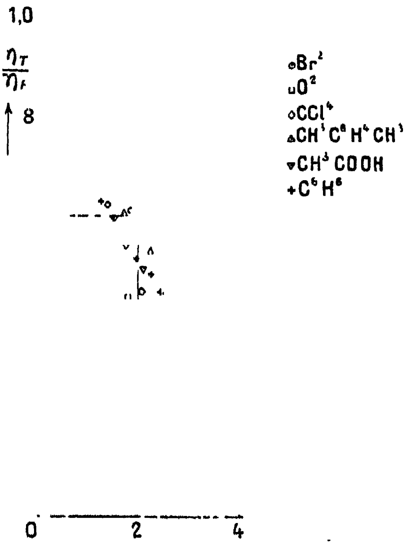

FIG. 5.

(*b*) Di-atomic Liquids.

The figures for Br_2 were calculated from experimental C_p, by combining the well-known thermodynamic formula for $C_p - C_v$ and our formulæ (2) and (3). The data for liquid-air were borrowed from the tables. The experimental data were insufficient for other liquids. It is remarkable that the curves for mono- and di-atomic liquids have the same general shape, but the difference of C_v's, for the same temperature, is about 2 calories, as it is for perfect gases.

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[2] L. Brillouin, *J. Physique*, 1936, 7, 153.

[3] A. Eucken and F. Hauck, *Z. physiak. Chemie*, 1928, **134**, 161.

6. Dynamical Properties of Liquids.

We sought to extend the former results to the viscocity and heat-conduction in liquids but it seems that for dynamical properties each liquid follows another curve (Fig. 5), where η_T/η_f (η = viscosity) is plotted against θ.

7. Summary.

Using a reduced temperature $\theta = \frac{T - T_c}{T_c - T_f}$, it is shown that the principal static properties of pure liquids follow with fairly good approximation one single law for all liquids. This shows us that it seems possible to construct an equation of state for liquids where the triple point temperature T_f is a constant of the same importance as the constants of van der Waals.

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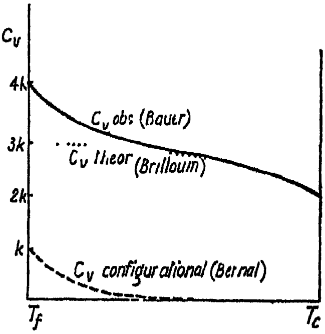
GENERAL DISCUSSION.

Professor J. H. Hildebrand (*Berkeley, Cal.*) said : The *ortho* and *para* disubstituted benzenes have very different melting-points, but nearly identical boiling points. If their densities should be found to differ by the extent this treatment would appear to demand it would be, to me, a very striking proof of its value.

With reference to the aberrent cases, I should like to point out that they all involve liquids in which hydrogen bonds are present.

Mr. J. D. Bernal (*Cambridge*) said : M.M. Bauer and Magat are to be congratulated for having produced such remarkable and far-reaching generalisations. It seems to me that the result of their work can be summed up most concisely by the statement, " There is only one simple liquid." However, such a general statement must be subject to several qualifications. In the first place it is fairly clear from the list of substances examined that, except for those substances which do not lie on the curve, all have molecules sufficiently symmetrical for us to be able to assume that in the liquid state they are rotating freely, for many of them, indeed, such free rotation already exists in the crystal state. In other words the general properties they have described are those of liquids with quasi-spherical molecules. It is not quite certain whether this class of molecules would include the liquid metals, over the whole range, or ionic liquids, though it is probably that for volume and compressibility these also would fall on the general curve. At first sight it is somewhat surprising that properties of liquids can be referred to two characteristic temperatures of which the freezing-point is one because it is generally agreed that the freezing-point in itself is not characteristic of the liquid structure and that in the absence of nuclei liquids undergo no significant changes either at the freezing-point or in the region near it. A paradoxical situation would for instance occur when a liquid has a number of different freezing-points for different crystalline modifications which of these ought to be used in the reducing expression. As a matter of fact the exact choice of the freezing-point is not very significant because from the shape of the expression it is extremely insensitive to the lower temperature chosen. The correct value to take would probably be something equivalent for the liquid to the Debye characteristic temperature of the crystal but it should be a value quite independent of whatever crystalline forms into which the liquid may be transformed. The character of the specific heat curve is one of peculiar interest. It appears that the specific heat at constant volume follows a curve which can be considered from the point of view expressed in my paper in conjunction with that of Professor Brillouin's paper. The normal curve for liquids would then be built up, as shown in Fig. 1, of two curves, one a value changing from $3R$ to $2R$ from about the region of the melting point to the critical point and the other the configurational specific heat of my theory which is large at low temperatures and practically disappears before the critical temperature is reached. Unfortunately the treatment of the specific heat at constant volume on my theory in its present form is not adequate to give the shape of this curve but it is at least plausible to attribute both the excess of Cv over $3R$ at low temperatures and its subsequent fall to configurational terms.



Generalised specific heat for curves for monatomic liquids.

FIG. 1.

Professor E. Bauer (*Paris*) said: Perhaps it is not necessary to suppose spherical molecules. The orientations of non-spherical ones are determined, just like their positions, by a repartition function which may have a universal character.

Dr. R. J. W. Le Fèvre (*London*) said: The effect of molecular rotation should be apparent in the relations between the dielectric constants of polar liquids and the reduced temperature, θ. Have the authors any data available on this point?

Professor F. Simon (*Oxford*) said: Liquids are certainly not of such a simple structure that all properties can be reduced to those of one single "ideal" liquid. It is sufficiently astonishing that one can find "reduced" formulæ for a number of properties, as has been shown in the paper by Bauer and Magat, and also for the process of melting by the formula mentioned in my paper. I believe, however, that it would be vain to try to represent *all* properties of a liquid in a reduced form.

Mr. F. C. Frank (*Oxford*) said: I do not think Dr. Bernal can fairly deduce that in all the liquids which fit Bauer, Magat and Surdin's normal curves the molecules are quasi-spherical by rotation. This is a possible interpretation, but another is that molecular shape has its influence upon liquid structure which, being related to its influence upon solid structure, is approximately measured and allowed for by the introduction of the fusion temperature into the authors' reduced equation.

Dr. E. Bauer (*Paris*), in reply, said: Since the meeting, we have plotted against θ all the available values for the volumes of *ortho*, *meta* and *para*-xylol. Those substances are the only ones for which we could find data. The experimental points (v. Hirsch[4]) fit very well with the mean curve, if one point is adjusted. The θ interval is unfortunately rather small, $\theta \sim 0{\cdot}5$ to $0{\cdot}8$. The experimental volumes[5] at 20° C. fit also very well for *ortho* and *meta*-xylol, but not at all for the *para* (difference about 10 per cent.). We have also tried to plot the dielectric properties against θ as suggested by Dr. Le Fèvre. We could not find any regularity.

Mr. Magat said: The boiling-point cannot be considered as a corresponding pressure for all substances. The question of hydrogen bonds is somewhat complex, in the H_2 case it does not seem to play a role. In what concerns H_2O Bernal and Fowler, and myself, have shown that the electrostatic forces and London forces explains the experimental results.

[4] *Wied. Ann.*, 1899, 69, 465, 466.

[5] *Landolt Börnstein*, I., 376.

THE VISCOSITY OF PURE LIQUIDS.

By A. G. Ward.

Received 5th August, 1936.

The properties of liquids can be divided into two classes according to whether they refer to the liquid in equilibrium or in process of change. To the first class belong the equation of state and the specific heats; the second class includes diffusion, rate of evaporation, conductivity for heat and electricity, and viscosity. Of these latter properties, the one in which experiment is most extensive and accurate is viscosity. It is evident that viscosity, in common with all the properties of a liquid, depends on the mass of the particles of which it is composed and the forces between the particles. It is, therefore, of some interest to endeavour to correlate the viscous properties both with other properties of the liquid, and with our knowledge of the forces between atoms, ions, and molecules provided by recent work on the liquid state, and on the forces in the solid state.

We shall consider solely the relation between viscosity and temperature, partly owing to the wealth of experimental material for the various types of liquid, and partly owing to the greater ease of theoretical treatment. The variation of viscosity with pressure,[1] with the electric field,[2, 3, 4] and with the magnetic field,[5] is now known for a small number of liquids, but these are almost all organic.

The Theory of Liquid Viscosity.

J. D. Bernal has shown [6] that the structure of a liquid can be represented by the mean co-ordination of one molecule or ion by other molecules or ions, and a measure of the deviation of the actual co-ordinations present in the liquid from this mean co-ordination. It is evident that the co-ordination of any one molecule or ion will change with time, under the influence of local stresses resultant from the Boltzmann distribution of the vibrational and rotational energy. If, then, we apply an external shearing stress, similar changes in the configuration of the liquid will occur. This process of shear will increase the extent of disorder in the liquid, which, after equipartition has been established between the configurational energy and the energy of vibration and rotation, corresponds to an increase in temperature. The energy necessary to produce this increase is provided by the work done by the shearing forces.

No attempt will be made to give a detailed picture of the mechanism by which the shearing stress is converted into a configurational change, but it is evident that a certain amount of energy (B k. cal. per gm. mol.)

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[1] P. W. Bridgman, *Physics of High Pressure*, 1931.

[2] R. O. Herzog, H. Kudar, and E. Paersch, *Physik. Z.*, 1934, **35**, 446.

[3] P. T. Sokolov and S. L. Sosinski, *Compt. r. Akad. Sci. U.R.S.S.*, 1935, **4**, 135.

[4] E. D. Alcock, *Physics*, 1936, **7**, 126.

[5] P. K. Raha and S. D. Chatterjee, *Ind. J. Physics*, 1935, **9**, 445.

[6] J. D. Bernal, *The Molecular Theory of Liquids*. This vol.

will be necessary to effect it. The number of ions or molecules with this energy is given by the Boltzmann law as proportional to $e^{-B/RT}$. The viscosity is inversely proportional to the number of molecules or ions with sufficient energy to bring about the configurational change necessary to relax the shearing stress, so the formula for the viscosity of a liquid becomes:

$$\eta = Ae^{B/RT} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

It is, perhaps inaccurate in this derivation to consider the distribution of thermal energy for the separate molecules or ions as instrumental in effecting the configurational change, but it is evident that if groups were considered the result expressed in (1) would remain unaltered.

It is next necessary to examine whether A and B are constants independent of the temperature and if not, we require to know how they will change with temperature. The value of B depends on the co-ordination of the molecules and ions in the liquid. If, then, the mean co-ordination remains invariant with the temperature, the value of B will be, to a first approximation, constant. If, on the other hand, the mean co-ordination changes with temperature, B will vary considerably with temperature. The changes in the value of A with temperature when B is a constant have been shown [21] to be small and will, for simplicity be neglected. When B is not constant it is probable that A changes too, so that we obtain the following equations:

B constant. $$\eta = Ae^{B/RT} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$B = B(T)$. $$\eta = A(T)e^{B(T)R/T} \quad . \quad . \quad . \quad . \quad (3)$$

Equation (2) was first derived by Guzman,[7] in 1913 and since then numerous modifications and derivations of it have appeared, the most important of which is that of Andrade.[21] This is obtained by substituting $A/v^{\frac{1}{3}}$ for A and c/v for B/R in equation (2) and improves the agreement with the experimental results. For our purpose the improvement, though appreciable, is not sufficient to justify the loss of simplicity, but serves to show that the invariance of B with temperature is a first approximation only. From the experimental results, the values of the constants A and B can be determined with sufficient accuracy by graphical methods utilising the linear relation between $\log \eta$ and $1/T$. Attempts have been made [16, 19] to find the form of equation (3), but these involve three or four constants and must be regarded as empirical equations. It is impossible to obtain the value of $B(T)$ at a given temperature from the experimental values for liquids for which equation (3) holds since the slope of the graph $\log \eta - 1/T$ is given by:

$$\frac{d(\log \eta)}{d(1/T)} = A'(T)f(T) + B'(T)F(T) + \frac{(B)T}{R}.$$

In Tables 1, 2 and 3 the values of A, B and the viscosity at the melting-point are given. In some cases rough values for B are given even when equation (2) does not hold, the accuracy of these values depends on the magnitude of $A'(T)$ and $B'(T)$. A full bibliography of the literature on the various forms of the exponential formula is given below,[7-31] and in addition Andrade's papers on the viscosity of liquids at their freezing-point are given.[20, 22]

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[7] J. de Guzman, *Anales de la Sociedad Espanola de Fisica y Quimica*, 1913, **11**, 353.

The Classification of Liquids.

A rational classification of liquids must depend on the types of force between the particles of which the liquids are composed. This can be effected from three points of view: (1) the presence or absence of permanent groups (molecules or complex ions) which cannot be treated as spherically symmetrical; (2) the presence or absence of directional forces; (3) the magnitude, and change of magnitude with distance of separation, of the forces between the particles.

Using the third criterion liquids are divided into ionic, homopolar, metallic and a class which we may call molecular. We can now apply the second criterion to these classes. Ionic liquids can then be divided according to whether the ionic links are highly polarised or not. If the polarisation is high the links will have a directional character. The homopolar class can only have directed bonds. The metallic class can be divided according to the electronic theory of metals, which confirms the results already obtained by crystal chemistry. The molecular class is subdivided into four groups by the types of force present, differing both in the magnitude of the forces and in their directional character. These are (a) London residual force, (b) dipolar, (c) hydroxyl bond, (d) hydrogen bond. The first criterion can then be used further to subdivide the groups in the ionic and molecular classes.

To determine the type of force present in a liquid use must be made both of the information available with respect to its constitution in the liquid state and also any relevant information concerning the forces present in the solid and the gas. The X-ray diffraction from liquids containing directional forces is usually distinctive. This is shown in the cases of both water [32] and methyl alcohol [33] where the presence of directional hydroxyl bonds has been demonstrated.

Tables I., II., and III., have been arranged according to this classification and illustrate its substantial applicability. Owing to the very variable nature of the strength of the metallic bond the various data for

[8] C. Drucker, *Z. physikal. Chem.*, 1918, **92**, 287

[9] J. Kendall and K. P. Monroe, *J. Am. Chem. Soc.*, 1917, **39**, 1799.

[10] C. V. Raman, *Nature*, 1923, **111**, 532.

[11] M. P. Venkatarama Iyer, *Ind. J. Physics*, 1930, **5**, 371.

[12] J. Frenkel, *Z. Physik*, 1926, **35**, 652.

[13] J. Frenkel, *Nature*, 1930, **125**, 581.

[14] J. Frenkel, *Acta Physicochimica U.R.S.S.*, 1935, **3**, 633.

[15] J. S. Dunn, *Trans. Faraday Soc.*, 1926, **22**, 401.

[16] E. W. Madge, *Nature*, 1930, **125**, 590.

[17] E. W. Madge, *J. Physic. Chem.*, 1930, **34**, 1599.

[18] E. N. da C. Andrade, *Nature*, 1930, **125**, 309.

[19] *Ibid.*, 582. [20] *Ibid.* 1931, **128**, 835.

[21] E. N. da C. Andrade, *Phil. Mag.*, 1934, **7**, 17, 698.

[22] *Ibid.*, 497. [23] S. E. Sheppard, *J. Rheology*, 1930, **1**, 208.

[24] S. E. Sheppard, *Nature*, 1930, **125**, 489.

[25] S. E. Sheppard, *J. Rheology*, 1930, **1**, 349.

[26] D. Silverman, *Trans. Faraday Soc.*, 1933, **29**, 1285.

[27] B. Prasad, *Phil. Mag.*, 1933, **7**, 16, 263.

[28] B. Prasad, *J. Ind. Chem. Soc.*, 1933, **10**, 143. [29] *Ibid.*, 1934, **11**, 913.

[30] H. Eyring, *J. Chem. Physics*, 1936, **4**, 283.

[31] D. B. McLeod, *Trans. Faraday Soc.*, 1936, **32**, 872.

[32] J. D. Bernal and R. H. Fowler, *J. Chem. Physics.*, 1933, **1**, 515.

[33] W. H. Zachariasen, *ibid.*, 1935, **3**, 158.

metals show large differences but a further subdivision is hardly justified by the amount of data.

TABLE IA.—IONIC LIQUIDS. NO DIRECTIONAL FORCES.*

	T_F.	T_B.	Δ	L_F.	L_B.	B.	A	η_F	Ref.
NaCl . .	1077	1712	0·59	7·22	44·3	9·10	2·11	14·0	34
NaBr . .	1028	1666	0·62	-	38·6	8·00	2·85	14·3	34
KCl . .	1045	1690	0·62	6·41	40·5	7·40	4·20	15·1	34
KBr . .	1003	1649	0·64		38·2	7·96	2·92	15·7	34
AgCl . .	728	1827	1·51	3·05	44·3	5·30	7·64	29·7	35
AgBr . .	703	-		2·37	-	4·85	11·7	37·8	35
AgI . .	825	-	—	-	—	5·15	15·8	36·5	35
$NaNO_3$.	581	--		3·69	--	3·68	12·2	29·14	36
KNO_3 .	606			2·58		4·38	7·9	29·85	36

TABLE IB. IONIC LIQUIDS. DIRECTIONAL FORCES.

	T_F.	T_B.	B_1.	B_2.	η_F.	
B_2O_3	294³		75·0	21·7	8×10^{12}	38
$LiNO_3$	528		4·1	—	68·4	36

* In Tables I., II., and III., T_F and T_B are the freezing-point and boiling-point respectively, and are given on the absolute scale. Δ is a measure of the range over which the substance is liquid and is given by $\Delta - T_B - T_F/T_F$. L_F and L_B are the latent heats of fusion and vaporisation in kilocalories per gram atom or gram molecule. The constant B from equation (1) is also given in these units. The value of A is such that viscosities calculated from equation (1) will be in poises (c.g.s. units). η_F is given, for convenience, in millipoises. The values of T_F, T_B, L_F, and L_B. have been taken either from the International Critical Tables or from Landolt-Bornstein's Physikalisch-Chemische Tabellen.

TABLE IIA.—METALLIC LIQUIDS. CLOSE-PACKED STRUCTURE.

		T_F.	T_B.	Δ.	L_F.	L_B.	B.	$A \times 10^4$.	η_F.	Ref.
1A	Na	370·5	1153	2·10	0·61	25	0·96	21·5	7·9	39, 40
1A	K	335·3	1033	2·08	0·57	21	1·15	9·75	5·5	39, 40
1B	Cu	1356	2573	0·90	2·75	116			37	41
1B	Ag	1233	2223	0·80	2·63	59·5	4·87	56·9	41·4	40, 42
2B	Zn	692·4	1180	0·71	1·74*	24	2·02	41·4	33·4	40
2B	Cd	593·9	1040	0·75	1·48	26	1·585	66·2	25·3	40
2B	Hg	234·2	630	1·68	0·57	14	0·598†	55·5†	20·1†	--
4B	Sn	504·8	2533	4·03	1·73*	78	1·603	41·3	20·3	43
4B	Pb	600·5	1803	2·14	1·31*	46	2·32	40·8	28·5	40, 41
5B	Sb	903·5	1653	0·83	2·92*	45	2·92	28·8	14·6	41
5B	Bi	544	1723	2·17	2·70*	46	1·715	38·2	18·6	43

* The values of Awberry and Griffiths (*Proc. Physic. Soc.*, 1926, **38**, 378 are probably the best available for these metals.

† The values for the viscosity of mercury were obtained for the range 0–100° C. by taking the mean of Erk's values (*Z. Physik*, 1928, **47**, 892) and a careful determination (E. C. Bingham and T. R. Thompson, *J. Am. Chem. Soc.*, 1928, **50**, 2878) which was published after Erk's review. These values are given :—

T°C.	0	10	20	30	40	50	60	70	80	90	100
$\eta \times 10^3$	16·85	16·13	15·49	14·98	14·53	14·07	13·69	13·33	13·01	12·71	12·45

TABLE IIB—METALLIC LIQUIDS. COMPLEX STRUCTURE

		T_F	T_B.	Δ.	L_F.	B_1.	B_2.	η_F	
3B	Ga	302 7	1873	5 20	1·33	0·855	1·25	210	11

TABLE III

	$\mu \times 10^{18}$	T_F	T_B			I_B.	B.	A.	η_F	
(a) Molecular Liquids. Non-polar.										
A .	0·0+	84·0	87·5	0·042	0·27	1·50	0·524	1·24	2·83	15
N_2 .	0·0	63·4	77·4	0·221	0·17	1·34	0·468	0·762	3·11	45
CO .	0·1	66·2	81·2	0·227	0·22	1·41	0·463	0·951	3·21	45
CH_4	0·0	89·2	111·8	0·254	0·24	2·20	0·740	0·347	2·25	46
O_2 .	0·0	54·8	90·2	0·645	0·106	1·67	0·406	1·945	8·00	45
C_2H_4	0·0	103·8	169·4	0·632	—	—	0·739	2·01	7·24	16
(b) Molecular Liquids. Dipolar.										
C_2H_5Br	1·85+	154·0	311·0	1·02		6·6	1·12*	6·25*	25	
CH_3I	1·65	206·9	315·6	0·66		6·5	1·12	7·11	11	
C_2H_5I	1·65	164·5	345·2	1·10		7·25	1·25	7·08	35	
C_3H_7I	1·65	161·6	375·4	1·32			1·41	6·54	55	
(c) Molecular Liquids. Hydroxyl Bond.										
H_2O .		273·0	373·0	0·37	1·43	9·65	3·05*	0·59*	18	
CH_3OH .	1·67+	175·2	337·5	0·92	0·53	8·4	1·84	2·49	50	
C_2H_5OH .	1·70	155·7	351·5	1·24	1·14	9·4	2·34	2·11	500	
C_3H_7OH .	1·66	146·0	370·8	1·54	—	9·9	3·16	0·97	5500	
C_4H_9OH .	1·66	183·2	390·7	1·13	2·22	10·4	3·46	0·72	1000	
$(CH_3)_3COH$	1·66	298·5	355·8	0·19	1·58	9·6	5·62	0·036	50	
(d) Molecular Liquids. Hydrogen Bond.										
HCOOH .	1·45+	281·4	373·5	0·33	2·70	5·8	2·49*	2·44*	21	
CH_3COOH	1·04	289·6	391·1	0·35	2·68	5·8	1·93	4·22	12	
C_2H_5COOH	0·88	251·0	414·1	0·65	—	7·6	1·78	5·12	19	

* For organic liquids there seemed little point in deriving highly accurate values for *A*, *B* and η_F, since all that was required was the order of magnitude for the various classes. So, using the specific volume at a single temperature, *A* and *B* were derived from the constants given by Andrade [81] The values of η_F were obtained either from the experimental results or roughly from equation (1).

+ All values of μ were taken from Freudenberg, *Stereochemie*, 1933

Departures from the Simple Exponential Formula.

We have already shown that in the case of liquids for which the co-ordination changes with the temperature the value of *B* in equation (1) will not remain constant but will change with the temperature. J. D. Bernal has shown that in liquids with directional forces the co-ordination increases with the temperature while in liquids without directional forces it is constant.[6] It seems probable that the change from a low to a higher co-ordination should render a configurational change of the type we have suggested easier since it weakens the binding in any particular direction. Hence we should expect *B* to decrease with

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[84] R. Lorenz, *Z. physikal. Chem.*, 1912, **79**, 63.

[85] R. Lorenz and A. Hochberg, *Z. anorg. Chem.*, 1916, **94**, 317.

[86] R. S. Dantuma, *ibid.*, 1928, **175**, 1.

temperature. The graph log η -- $1/T$ for boron trioxide (Fig. 1) and the values of B at low and high temperatures given as B_1 and B_2, in Table IB show that even allowing for the errors in evaluating B_1 and B_2, B must decrease with the temperature. In boron trioxide we have a highly polarised ionic bond as has been shown by the crystal structure and by the difficulty of inducing crystallisation.[37] In the case of those alcohols where the hydroxyl bond plays a predominant part in determining the configuration of the liquid (and in the solid, as shown by the high melting-point) a similar large change in B occurs. In water it is probable that some weakening of the bonds occurs in addition to the change in co-ordination,[6] but the large change from 0–50° C. in the slope of the graph (Fig. 2) as compared with the change from 50–100° C. suggests that the latter is the predominant effect. Water is of particular importance as there is direct X-ray evidence for the change in co-ordination.[32] It is of importance to note that in liquids with directional forces, not only the co-ordination of nearest neighbours is of importance, but also the co-ordination of next nearest neighbours, as shown by the case of water.

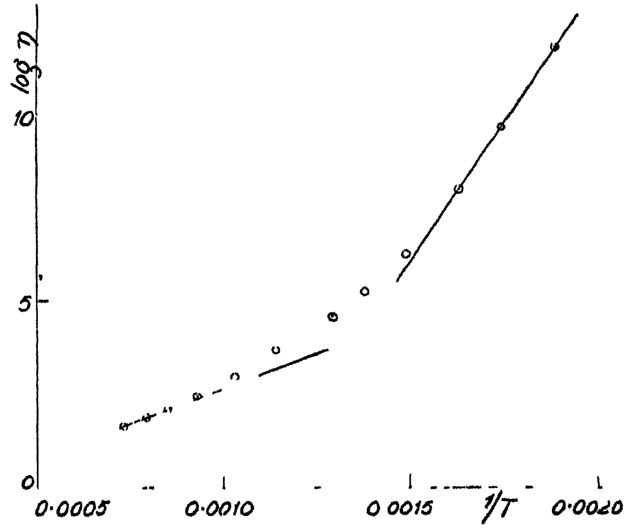

FIG. 1. - Graph log η — $1/T$ boron trioxide.

The change in structure of these liquids with directional forces, does not involve any change in the type of forces present. There are, however, two changes which may take place in a liquid which cause a change in the type of force present and so result in a departure from the exponential formula.

The first of these consists of the dissociation of weakly bound molecules. By molecule is meant an aggregate which persists for a time long compared with the time involved in the relaxation of the viscous stresses. The dissociated atoms or molecules will interact more than when combined, so the value of B will increase with the number dissociated. In general this means B will increase with temperature. The most striking instance of this is gallium. In the solid there are groups of two atoms which may be said to constitute a molecule.[47, 48] These molecules persist in the liquid, as is shown by the X-ray diffraction pattern.[49] As the temperature increases it is probable that these molecules break up and the liquid becomes more similar to the close packed metals. Correspondingly we find a very low value of B near the melting-point, 0·855 k. cal. per gm. mol. and an appreciably higher value at high temperatures, 1·25 k. cal. Formic acid provides another instance of this type of departure but the bond in the higher organic acids is so strong that it is not broken even at the boiling-point, the vapour consisting partly of double molecules.

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[37] N. W. Taylor and S. S. Cole, *J. Am. Chem. Soc.*, 1934, **56**, 1648.
[38] G. S. Parks and M. E. Spaght, *Physics*, 1935, **6**, 69.
[39] F. Sauerwald, *Z. Metallkunde*, 1934, **26**, 259.
[40] K. Gering and F. Sauerwald, *Z. anorg. Chem.*, 1935, **223**, 205.
[41] A. Bienas and F. Sauerwald, *ibid.*, 1927, **161**, 51.
[42] W. Radecker and F. Sauerwald, *ibid.*, 1931, **203**, 156.
[43] F. Sauerwald and K. Topler, *ibid.*, 1926, **157**, 117.
[44] K. E. Spells, *Proc. Physic. Soc.*, 1936, **48**, 299.
[45] N. S. Rudenko and L. W. Schubnikow, *Physik. Z. Sowjetunion*, 1934, **6**, 470.
[46] *Ibid.* 1935, **8**, 179.

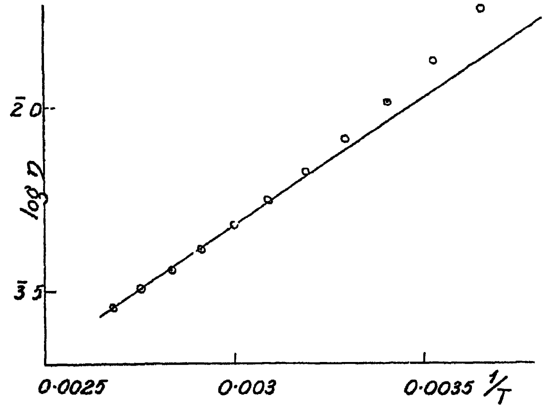

Fig. 2.—Graph $\log \eta - 1/T$ water.

The second kind of change in the type of force present results from the commencement of rotation of groups previously linked by directional forces. Initially librational motion will weaken the directional forces and with the commencement of free rotation they will vanish. In this case we should expect a fairly high value of B at low temperatures, a period of transition in which the slope of the curve $\log \eta$ $1/T$ ceases to give any measure of B owing to the large value of $B'(T)$, and finally a value of B lower than the initial value. It is probable that many of the dipolar liquids would show this effect at low temperatures, but the only substance for which measurements are available which shows anomalies probably due to

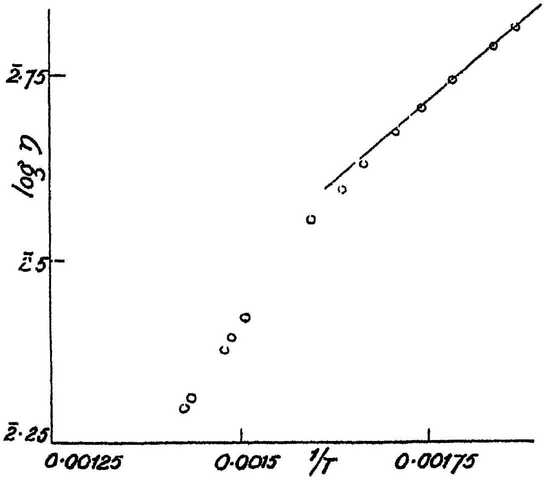

Fig. 3.—Graph $\log \eta - 1/T$ lithium nitrate.

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[47] F. Laves *Z. Krist.*, 1933, **84**, 256.
[48] A. J. Bradley, *Z. Krist.*, 1935, **91**, 302.
[49] F. Sauerwald and W. Teske, *Z. anorg. Chem.*, 1933, **210**, 247.

this cause, is lithium nitrate (Fig. 3). The nitrate ion is certainly in free rotation in fused potassium and sodium nitrates, and, allowing for the temperature of melting, they have normal values for the viscosity at the melting-point compared with sodium chloride. Lithium nitrate has a value more than twice as high, but only a slightly lower melting-point than the sodium salt. In addition the lithium ion is highly polarising. The shape of the graph is in agreement with the theory but measurements are not available to sufficiently high temperatures to confirm that the final value of B is less than the initial value.

The examples given here include all the cases of large departures from the exponential law so that we may conclude that in liquids obeying the law the structure remains fundamentally unchanged on changing the temperature and that B is largely unaffected by the extent of disorder in the liquid.

The Relation between B and the Latent Heats of Fusion and Vaporisation.

Guzman[7] first showed that there is a rough correspondence between B and the latent heat of fusion but we are now able to give a theoretical basis for this correspondence and also to account for many cases where it no longer holds. J. D. Bernal[6] has shown that melting involves the change from the configuration of the solid to that of the liquid and distinguishes two cases, one in which the structure of the liquid is merely a disordered form of the structure of the solid, and the other in which the structures are fundamentally different. It is evident that the latent heats in the two cases will be very different, being small in the first case and large in the second. Now the configurational change which we have used to account for liquid fluidity is of the same type as that involved in the first type of melting though not identical. So we should expect the ratio B/L_F to be approximately constant for liquids of the same structural type when no change of co-ordination occurs on melting. Thus for sodium chloride and potassium chloride the ratios are 1·26 and 1·17. Similarly for the metals with a close packed crystal structure and argon we get the figures: Na, 1·57; K, 2·01; Ag, 1·85; Pb, 1·76; A, 1·94. Considering the inaccuracy of the values of B and of L_F, we may say that the ratio is constant within the experimental error. For the metals which depart from the close packed structure the latent heat is always high, corresponding to the energy change involved in the transition to a lower co-ordination lattice.

There is little reason to expect any close correspondence between B and the latent heat of vaporisation except in the case of the molecular liquids where the forces between molecules in the vapour phase are the same as those in the liquid (except where the hydroxyl bond and hydrogen bond are of importance in the liquid structure). It is seen that there is quite a close correlation between the figures, B being large when L_B is large.

The Magnitude of B and η_F.

(a) Ionic Liquids.

Ionic liquids all have high values of B, which is to be expected, since the configurational change probably involves a partial breakdown and rebuilding of the co-ordination of an ion by ions of the opposite polarity.

It seems probable that the value of B will depend on the sum of the ionic radii, so that when the sum is large B will be small. This is in agreement with the results for the alkali halides, except that B for potassium chloride is less than for potassium bromide. This deviation is probably due to experimental error. It is of interest to note that the values of η_F are, within experimental error, the same. The much higher value of η_F for the silver compounds, at least in the case of the chloride, is due to the low melting-point. The high temperature modification of silver iodide has been shown to consist of close packed iodine atoms with the silver atoms, not in fixed positions, but free to move through the iodine lattice.[50] It is evident that the silver atoms will not contribute to the value of B in the same way as sodium in sodium chloride. Silver chloride will resemble most closely sodium chloride and correspondingly we find B greatest in this case. In silver iodide the interaction between the iodine atoms will be greater than between bromine atoms in the bromide. This, together with a probable change in co-ordination from 6 : 6 to 4 : 4 accounts for the higher value of B for the iodide. It is of interest to note that the melting-point of the bromide is the lowest of the three, and also that the latent heat of fusion of the bromide is less than that of the chloride. The low values of B and the melting-point for sodium and potassium nitrates indicate that the interaction between the metal ions and the rotating groups is less than with an ordinary monatomic anion.

(b) Metallic Liquids.

The values of B, since all the liquids in Table IIA are close packed in the liquid state, give a measure of the magnitude of the interaction between the metal atoms. η_F is given quite accurately by the Andrade formula for those liquids which are either close packed in the solid or nearly so.[20, 22] Since T_F is involved in the formula and this temperature, for the formula to hold, must apply to the transition close packed liquid to close packed solid, it is not surprising that when the solid structure departs considerably from close packing appreciable deviations occur.

(c) Molecular Liquids.

The non-polar liquids have very low values of B corresponding to the small interaction between the molecules. The very low value of B for oxygen may be due to the presence of O_4 molecules. It is of interest to note the close resemblance between nitrogen and carbon monoxide which have the same molecular weight and the same number of electrons.

In the case of dipolar liquids it is probable that rotation is preventing effective interaction between the dipoles. This is confirmed by the marked increase in viscosity of these liquids on subjecting them to an electric field.

Trimethyl carbinol, and to some extent methyl and ethyl alcohols, depart from the exponential formula as we have already described. The other primary alcohols obey the formula quite well but the high value of B and of the viscosity at the melting-point (compared with the dipolar liquids) show that the configurational change in viscous shear involves a breaking of hydroxyl bonds. It may be that the length of the chain exerts a steric influence and prevents a change of co-ordination with temperature. This is in agreement with the fact that those alcohols with fairly symmetrical molecules depart most from the exponential formula.

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[50] L. Strock, *Z. physikal. Chem.*, 1934, B, **25**, 441.

We have already seen that formic acid departs from the exponential formula while the other fatty acids do not. The explanation given accounts for its other anomalous properties.

Summary.

We may summarise the conclusions as follows :—

1. No structural change with temperature of a type involving either an alteration in co-ordination or a change in the kind of force present, occurs in liquids obeying the exponential formula for the relation between viscosity and temperature.
2. There is a close resemblance between the configurational changes involved in melting and viscosity.
3. For liquids of the same structural type in which the change solid-liquid corresponds only to a transition from order to disorder, the ratio B/L_F is constant.
4. The magnitude of B depends on the co-ordination and on the inter-ionic, interatomic or intermolecular forces.

I should like to acknowledge a considerable debt of gratitude to J. D. Bernal for the general viewpoint on the solid and liquid states, and for his assistance and encouragement in the work described above.

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INTERMOLECULAR FORCES OF NORMAL LIQUIDS.

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In general the volumes and specific heats of liquids are but slightly different from those of the same substance in the solid state. It is therefore to be expected that the laws of force between two atoms not chemically combined would be the same in both states.

The modern theory of the specific heats of solids uses the concept that at some specific distance, l_0, between the centres of gravity of monatomic molecules the resultant force between them is zero. Closer approach than this produces a repellant force which increases in magnitude as the distance apart decreases; greater separation produces an attractive force which, *at first*, increases as the distance increases. On the other hand, consideration of compressed gases and of liquids at their critical point shows that this attractive force is rapidly *diminishing* with the distance apart when this is comparable with $2l_0$ or even less. One is therefore compelled to suppose that in a liquid, such as carbon tetrachloride for example, the forces holding the molecules together will be mainly those of adjacent atoms, *i.e.* between a chlorine of one molecule and a chlorine of another, rather than any forces between two carbon atoms, or between a carbon atom of one molecule and a chlorine of another.

This suggests that for complex molecules as well as monatomic ones there should be some distance, l_0, at which two molecules would be without effect on one another and that the variation of force with distance should be a function of $l - l_0$ rather than of l itself. For symmetrical molecules l_0 would be constant, but for unsymmetrical ones it would vary with the relative positions of the molecules.

Such a conception seemed to be very different from the classical van der Waals' treatment and, in order to determine whether the properties of liquids could be interpreted upon these lines, a law of force was postulated and the consequences explored, with rather remarkable results.

It seemed that the most appropriate form of the law would be: $f = a(l - l_0)e^{-b(l-l_0)}$ where f is the force, positive when attractive and negative when repellant; l is the distance between the centres of gravity of the two molecules concerned; and a, b, and l_0 are specific constants, the latter with the significance already indicated.

This equation could be directly tested if compressibility data at the absolute zero of temperature were available. For if we consider a cube containing one gram of the substance, the force, F, on the face of this cube would be proportional to f, and the length of the cube side, L, would be proportional to l, hence $F = \alpha(L - L_0)e^{-\beta(L-L_0)}$ where α and β are specific constants. Then

$$\ln . F = \ln . \alpha + \ln . (L - L_0) - \beta(L - L_0).$$

Consequently log $F/(L - L_0)$ should be a linear function of L.

The influence on this of the thermal agitation of the molecules at finite temperatures was not obvious, but it was hoped that the effect might be negligible at high pressures. Accordingly the data of Bridgman [1] at pressures of 1000 to 12,000 atmospheres were used for the test. Only relative volumes are given but this merely affects the constants. $L = V^{\frac{1}{3}}$, $F = L^2P$, and for L_0 the value of L at zero (or unit) pressure at the particular temperature concerned is employed and denoted by L'.

The anticipated linear relationship is found, as shown in Figs. 1 and 2, in the case of normal liquids such as carbon bisulphide, ether, ethyl bromide and phosphorus trichloride, but not with abnormal liquids such as water or acetone.

The value of $F/(L' - L)$ in the limit when $L' = L$ can be calculated from ordinary compressibility data at low pressures being equal to $3L'/\beta'$, where β' is the coefficient of compressibility (not the β of the above equation). The result may be compared with that obtained from extrapolation of the graph as has been done in the two cases for which data were available from the measurements of Tyrer.[2] As will be seen on the graphs the extrapolated value agrees perfectly with the calculated in the case of carbon bisulphide at 20° C. and is a little high in the case of ether at the same temperature.

While these results are not entirely unambiguous they do suggest that the equation is of the right form and attention was then directed to the question of thermal expansion.

Two molecules whose centres of gravity are separated by a distance l_0 exert no resultant force upon one another. If they oscillate, let the distance of nearest approach be $l_0 - y$ and denote the potential energy with respect to one another at this point by E_y. Let the distance of furthest separation be $l_0 + z$ and denote the potential energy by E_z. Since E_y must be equal to E_z it follows from the form of the equation that z is greater than y. Moreover at distances greater than l_0 the field of force is slightly less than it is at distances correspondingly less than l_0.

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[1] *International Critical Tables*, vol. 3, 40-42.

[2] *J. Chem. Soc.*, 1914, 105, 2534.

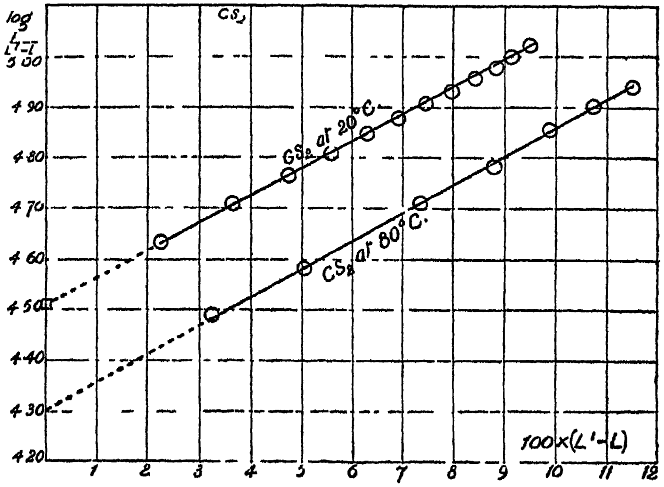

FIG. 1.

Therefore the molecules will be moving slightly more slowly when at a given distance greater than l_0 than they will when moving at the same distance less than l_0. This, together with the fact that z is greater than y, results in the average distance apart being greater than l_0, say $l_0 + x$.

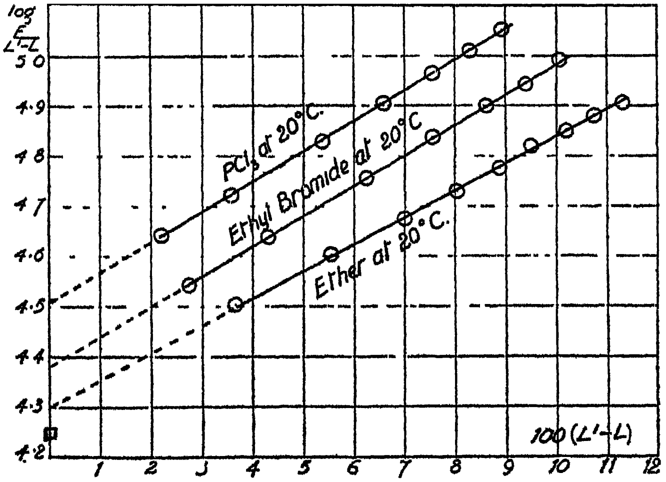

FIG. 2.

No rigid mathematical proof of the resulting effect on an assemblage of molecules has yet been achieved, but certain probable postulates have yielded such remarkable results that it is felt they cannot be far from the truth. They are: (1) That in this case also (in the absence of appreciable pressure) the average distance of closest approach between two molecules, $l_0 - y$, and the average distance of furthest separation, $l_0 + z$, are such that $E_y = E_z$. (2) That the mean distance between molecules will be, as symmetry suggests, $l_0 + (z - y)/2$, which will be denoted by $l_0 + x$. (3) That the energy required to drive two molecules from their mean distance, $l_0 + x$, to the average distance of closest approach, $l_0 - y$, will be proportional to the thermal energy per degree of freedom and therefore also proportional to the absolute temperature.

The integral $\int_{l_0}^{l} f \, . \, dl$ is $\frac{a}{b^2}[1 - \{1 + b(l - l_0) \, . \, e^{-b(l-l_0)}\}]$.

It is convenient to transpose this equation by writing $(l - l_0)/l_0 = -Y$ when l is less than l_0 and $= Z$ when l is greater than l_0, and introducing $A = al_0$ and $B = bl_0$. Then the potential of approach is

$$\frac{Al_0}{B^2}[1 - \{1 - BY\}e^{+BY}] = \frac{Al_0}{B^2}\psi'_{BY}$$

where ψ'_{BY} represents the term in brackets, and the potential of separation is $\frac{Al_0}{B^2}[1 - \{1 + BZ\}e^{-BZ}] = \frac{Al_0}{B^2}\psi_{BZ}$ where again ψ_{BZ} represents the term in brackets.

A table of values of ψ'_{BY} was worked out to five figures for intervals of 0·01 from 0·01 to 1·00 of BY and from a similar table for ψ_{BZ} the values of BZ such that $\psi'_{BY} = \psi_{BZ}$ for each value of BY were determined. The term BX, proportional to the mean distance of separation, x, $(X = x/l_0)$ was then obtained from the relation

$$BX = \tfrac{1}{2}(BZ - BY).$$

Finally, $E_{BY} - E_{BX}$ is given by

$$\frac{Al_0}{B^2}(\psi'_{BY} - \psi_{BX})$$

and for convenience the term in brackets is denoted by χ.

This provides a table of values of BX (proportional to $L - L_0$) which corresponds according to the theory with the given values of χ (proportional to the absolute temperature). A plot of log. BX against log. χ is shown in Fig. 3 and it is observed that χ has a critical value which in fact occurs when $\chi = 0{\cdot}5243$ (log. $\chi = \bar{1}{\cdot}71958$). This should correspond to the critical temperature

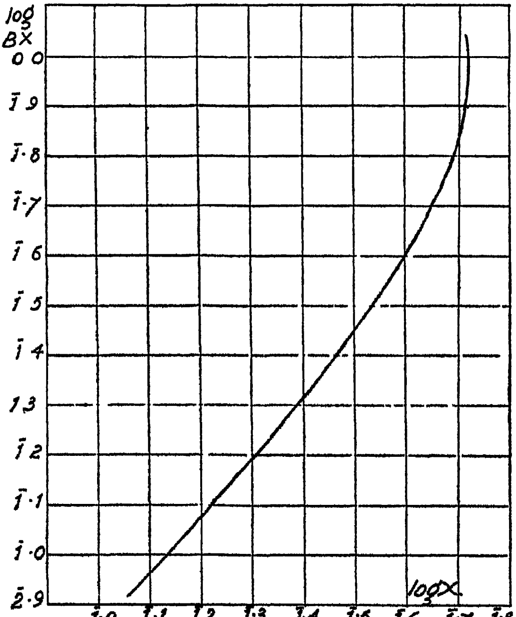

FIG. 3.

and thus fixes the factor of proportionality between χ and T. For any value of T, $\chi = 0{\cdot}5243T/T_c$. Then from the tables it is possible to determine (by interpolation if necessary) a value of BX for any value of T. It only remains to determine whether any value of L_0 can be chosen which will give a constant ratio between BX and $(L - L_0)$ at all temperatures.

Ether may be chosen in illustration. In this case $T_c = 466{\cdot}9$ K. Log. $T_c = 2{\cdot}66922$ and log. $\chi_c = \bar{1}{\cdot}71958$ so at any temperature log. $\chi =$ log. $T - 2{\cdot}94964$. The data of Timmermans [3] were employed for the density of ether and $L = (1/D)^{\frac{1}{3}}$. The value of L_0 was chosen arbitrarily as 0·9975. For the temperatures given (in degrees centigrade) the values of log. $(L - L_0)$ − log. BX are :—

t		t	
15·1	$\bar{1}$·6061	− 53·6	1·6056
0·0	$\bar{1}$·6064	− 63·6	$\bar{1}$·6072
− 6·2	1·6070	− 74·25	$\bar{1}$·6072
− 13·1	$\bar{1}$·6063	− 83·4	$\bar{1}$·6057
− 22·95	$\bar{1}$·5958	− 94·5	$\bar{1}$·6058
− 30·6	1·6061	− 100·85	$\bar{1}$·6064
35·3	$\bar{1}$·6056	− 111·6	$\bar{1}$·6071
− 37·2	1·6067	− 116·2	1·6062
− 45·0	1·6065	− 123·3	$\bar{1}$·6068

Such close concordance over so wide a temperature range is remarkable, particularly in view of the fact that there is only one constant, L_0, to be chosen arbitrarily. It makes it very difficult to believe that the agreement is merely fortuitous.

Taking log. $(L - L_0)$ − log. $BX = \bar{1}{\cdot}6060$, we have $L - L_0 = 0{\cdot}4036$ BX. Remembering that $X = (L - L_0)/L_0$ and that $L_0 = 0{\cdot}9975$, $B = 0{\cdot}9975/0{\cdot}4036 = 2{\cdot}472$.

From this the magnitude of the postulated vibrations may be judged. At 0° C., $\chi = 0{\cdot}30668$, $BZ = 1{\cdot}20097$, and $BY = 0{\cdot}65643$. With the above value for B it is seen that $Z = 0{\cdot}4857$ and $Y = 0{\cdot}2656$. Thus the average distance of closest approach is 73·44 per cent., and that of furthest separation is 148·5 per cent., of l_0, although the mean distance apart is only 111 per cent.

At higher temperatures (above 100° C.) the agreement becomes much less. Using the density data of Young [4] the values of log. $(L - L_0)$ − log. BX are 1·6076 at 100° C.; 1·6249 at 150° C.; and 1·7705 at 193·8° C. (the critical temperature). Thus the error in the ratio (not the log) is 4½ per cent. at 150° C. and 46 per cent. at the critical temperature. But according to the theory the average distance of maximum separation is, respectively, nearly twice and three times l_0 at the two latter temperatures and when vibration carries the molecules as far apart as this the second postulate can hardly be expected to hold.

*Iso*pentane may be chosen as a second example to illustrate an alternative method of calculation in which the constant ratio between $(L - L_0)$ and BX is arbitrarily chosen and a value for L_0 calculated for each temperature. The density data are again taken from the work of Timmermans.[3] Temperatures are given on the absolute scale.

T	L_0	T	L_0
288·1	1·0446	209·8	1·0448
273·1	1·0444	198·85	1·0449
266·9	1·0444	189·7	1·0448
260·1	1·0447	178·6	1·0445
250·15	1·0447	168·25	1·0445
242·15	1·0445	161·7	1·0444
237·8	1·0445	156·9	1·0444
228·1	1·0446	130·6	1·0435
219·5	1·0446	115·00	1·0425

The result with ethyl bromide is slightly less good, the ratio $BX/(L - L_0)$ ranging from 2·867 to 2·909 over the temperature range — 100° to 20° C. With phosphorus trichloride the same ratio varies from 0·5893 to 0·5955 over the temperature range — 80° to 0° C.

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[3] *Proc. Roy. Dub. Soc.*, 1912, **13**, 310.

[4] *Ibid.*, 1910, **12**, 374.

TABLE.

BY.		χ.
0·41	0·07823	0·10806
0·42	0·08292	0·11309
0·43	0·08781	0·12011
0·44	0·09291	0·12641
0·45	0·09824	0·13290
0·46	0·10377	0·13957
0·47	0·10950	0·14642
0·48	0·11550	0·15345
0·49	0·12174	0·16068
0·50	0·12823	0·16808
0·51	0·13498	0·17568
0·52	0·14198	0·18345
0·53	0·14927	0·19141
0·54	0·15687	0·19952
0·55	0·16479	0·20785
0·56	0·17301	0·21635
0·57	0·18156	0·22503
0·58	0·19044	0·23387
0·59	0·19973	0·24288
0·60	0·20939	0·25203
0·61	0·21947	0·26140
0·62	0·23000	0·27090
0·63	0·24089	0·28053
0·64	0·25232	0·29031
0·65	0·26422	0·30011
0·66	0·27665	0·31028
0·67	0·28963	0·32045
0·68	0·30322	0·33066
0·69	0·31743	0·34106
0·70	0·33229	0·35149
0·71	0·34786	0·36199
0·72	0·36421	0·37253
0·73	0·38134	0·38310
0·74	0·39938	0·39367
0·75	0·41836	0·40421
0·76	0·43831	0·41470
0·77	0·45938	0·42510
0·78	0·48163	0·43540
0·79	0·50522	0·44552
0·80	0·53019	0·45539
0·81*	0·5568	0·4651
0·82	0·5851	0·4743
0·83	0·6156	0·4831
0·84	0·6480	0·4914
0·85	0·6826	0·4993
0·86	0·7200	0·5064
0·87	0·7608	0·5125
0·88	0·8053	0·5176
0·89	0·8537	0·5215
0·90	0·9075	0·5238
0·91	0·9675	0·5242
0·92	1·0346	0·5223

* From the method of compilation values from here on are subject to small errors in the fourth decimal place.

It is not to be supposed that the molecules are necessarily regarded as rigid on this theory. Such great variations in the distance between the centres of gravity, especially of approach, on the contrary argue considerable deformation. This effect is, however, included in the formula. The approach of two chlorine atoms which are parts of different molecules of carbon tetrachloride, expressed in terms of the centres of gravity of these molecules, is no doubt very different from the approach of two atoms of chlorine which are parts of different molecules of liquid chlorine expressed in terms of the distance between the centres of gravity of *these* molecules. The sheer magnitude of the Y term suggests that the whole effect cannot be due to the difference between the centres of gravity of the chlorine atoms themselves with rigid molecules behind them. The terms, however, seem to compound in such a way as to allow the formula to give such wonderful results.

Accordingly in estimating the number of degrees of freedom involved we have to take into account not only the movement of the molecule as a whole, the rectilinear motion of the centre of gravity, but also the vibrational energy. Thus if the number of contacts in an assemblage of molecules (say one gram molecule) be n, then the thermal energy associated with the movements considered must be $6T$ calories, one calorie per degree of freedom per degree of temperature. The energy of rotation need not be considered since the assumption was that l_0 was the same in all directions. Therefore the total energy involved is $na\chi/b^2 = 6T$. Hence

$$na/b^2 = 6T/\chi = 6T_c/0·5243.$$

But the work necessary to separate two molecules (one contact) to infinity is a/b^2 Hence the work necessary to separate all the molecules of one gram molecule to infinity would be $na/b^2 = \lambda_0$, the internal latent heat at the absolute zero of temperature. Combining this with the relation given above, $\lambda_0/T_c = 6/0·5243 = 11·45$. Now usually $T_c = 1·7T_B$, where T_B

is the boiling temperature, hence $\lambda_0/T_B = 19{\cdot}5$. This may be compared with Trouton's rule according to which $\lambda_B/T_B = 20{\cdot}7$.

These numerical agreements seem to indicate that the basic assumptions are on the right lines and invite the attention of the mathematical physicist.

Summary.

A law relating the force between molecules to the distance separating them is postulated and it is shown that the compressibilities of normal liquids at high pressures appears to confirm it. On certain probable postulates as to the statistical consequences in an assemblage of molecules a general relation is deduced between a term which should be proportional to the absolute temperature and another which should be proportional to the thermal expansion. This is found to fit the experimental data for normal liquids with great accuracy over a temperature range from the melting-point to about fifty degrees short of the critical temperature with only one constant to be arbitrarily fixed. Moreover the theory gives rise to a law similar to Trouton's rule and of approximately the same magnitude.

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GENERAL DISCUSSION.[*]

Professor J. Kendall (*Edinburgh*) said : The valuable list of references to equations connecting the change of liquid viscosity with temperature, at the end of this communication, omits the derivation of Arrhenius: $d \log \eta \,.\, v^{\frac{1}{3}}/dT = K/T^2$. Although this was not published until 1918,[5] it was actually worked out in 1912, before Guzman's equation (which is generally accorded priority) had appeared in the literature.

Dr. R. J. W. Le Fèvre (*London*) said: How are "normal" and "abnormal" liquids defined? It would be interesting to know the names (or types) and numbers of liquids which have been found to fall into the two classes.

Dr. L. Brillouin (*Paris*) said: In the kinetic theory of gases there appears a relation between viscosity ζ and heat conductivity κ; in liquids, these two phenomena should also show some sort of connection, as they both derive from a common origin. I tried some years ago[6] to build up a theory of the viscosity for liquids, but this attempt was not very successful. It led, however, to following law, which is not very far away from experimental results:

$$\frac{\partial \zeta}{\partial t} = -\frac{5}{3}\frac{J\kappa}{W^2};$$

ζ viscosity; κ heat conductivity; J mechanical equivalent of heat; W velocity of sound.

Mr. J. D. Bernal (*Cambridge*) said: The data in Mr. Ward's paper can be used to bring out some striking regularities between liquids in the different classes into which he divides them. If we take the value of $\frac{B}{T_m}$ which might be called the viscosity entropy of the liquid, we find that in each class we have substantially similar values. Thus among the ionic liquids it varies only between 0·085 and 0·062. There is a very similar range of variation between 0·083 and 0·062 in the case of the molecular liquids, but in the metallic liquids the values are only half as great, ranging between 0·042 and 0·024. It is fairly clear that for viscosity as well as for other properties we can consider two sharply defined types of liquid, corresponding physically to a greater or smaller degree of resemblance to the crystalline state. In the case of the molecular and metallic liquids this is in turn due, as pointed out in my paper, to the effective range of the inter-molecular forces, the long range of the metallic forces leading to a more regular arrangement and consequently to a smaller viscosity entropy. The case of the ionic liquids is more complicated. Here the restriction that any re-arrangement should leave positive ions surrounded by negative ones must act to compensate for the greater range of interionic forces and the resemblance of the values to those of molecular liquids is probably fortuitous.

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[*] On two preceding papers.

[5] *Medd. K. Vetenskaps. Nobelinstitut*, 3, No. 20.

[6] *J. Physique*, 1922, 3, 326 and 362.

The simple and beautiful regularities set out in Mr. Hudleston's paper seem to me to follow from the general conclusions already apparent in Professor Bauer's paper, namely, that there is only one liquid, or at any rate, that the properties of all molecular liquids with quasi-spherical molecules are essentially similar. In my view the compressibilities of liquids cannot be simply explained by treating them as the coming closer together of individual molecules in any kind of force field. A large part of the compressibility will be due to the change of molecular configuration which will be related in a more complicated way to the inter-molecular forces. Mr. Hudleston has not explicitly considered this effect. He has, in fact, used a theory based on simple assumption of inter-molecular potential expressed in the rather unusual form of intermolecular force, and yet has arrived at expressions which fit observations for most liquids very exactly. This is probably due to the fact that the configurational compressibility term for all liquids having the same structure is the same ratio of the intermolecular compressibility and this ratio appears implicitly in his equations. Similar considerations apply to the case of thermal expansion. The irregularities he has observed here are clearly the same as those discovered in a purely empirical way by Bauer and Magat and also, in my view, depend upon the fact that the configurational thermal expansion is simply related to the corresponding anharmonic vibration expansion of crystals.

Mr. A. G. Ward (*Cambridge*), in reply, said : It is probable that further information concerning the structure of liquids can be obtained by a comparison of measurements of the various dynamic properties. In particular, since all dynamic properties must involve a configurational change, there should be relations between the constants B for such properties as obey the relation :—

$$\phi = Ae^{B/RT}.$$

These relations will be similar in type to that between the term B for viscosity and the latent heat of fusion.

Mr. L. J. Hudleston (*Aberystwyth*), in reply to a question, said : The value of β obtained from compressibility measurements is not the same as that of B obtained from the thermal dilatation. This is because in the latter case we are measuring in general the force set up by the approach of two molecules which are free to distort, whereas in the former we are measuring the force arising by the approach of two molecules which are simultaneously under stress from both directions at right angles to the line between their centres and therefore are less easily distorted. It appears that β is approximately the cube of B in the cases considered.

THE DETERMINATION OF STRUCTURE IN LIQUIDS BY X-RAY METHODS.

By J. T. Randall, M.Sc.

(Communication from the Staff of the Research Laboratories of the General Electric Company, Limited, Wembley, England.)

Received 31*st August*, 1936.

The object of this paper is to give some indication of the present position in regard to the determination of structure in liquids by X-ray methods. Complete summaries have been made in recent years by several authors, and the method of the present article is rather more eclectic in selection of examples. In addition to known procedures, an outline is given of a modification of the Debye Fourier Inversion formula which renders absolute determinations possible in certain cases.

The first recorded experiments on the diffraction of X-rays by liquids are those of Debye and Scherrer in 1916 [1] in which two very important features were recorded: the diffuse nature of the pattern on the X-ray photograph and the establishment of the phenomenon as one of interference. The improvement of experimental technique shortly after the war resulted in the observation of secondary haloes by Keesom and de Smedt [2] for oxygen, argon, and nitrogen, in the liquid states. The third feature was made clear by Hewlett [3] when he showed by use of the ionisation-spectrometer method, that the scattering at small angles is small. The work of Keeson and de Smedt had already indicated that the phenomenon existed for such so-called "monatomic" liquids as argon, and for the obviously molecular liquids such as benzene. Microphotometer records of patterns for water and liquid rubidium are shown in Figs. 1 and 2 in illustration of these points. Subsequent to this several more or less unsatisfactory theoretical attempts were made to account for the patterns. A complete discussion of these has been given elsewhere.[4]

Stewart's [5] work has been of great value in showing, in very many instances, similarities between the patterns in the liquid and solid states. This led him to suggest the conception of groups, or cybotaxis, in liquids; similar suggestions had been made some years before in a rather cruder form by Hewlett [3] and Keeson and de Smedt.[2] Stewart argues that catastrophic changes in atomic and molecular forces at the melting-point are unlikely to be the rule and that temporary groupings of molecules over small elements of space and time are probable. It is not necessarily true however, that the type of grouping shall always be the same in the solid and liquid states; in bismuth for example the liquid is distinctly different from the solid.[6] That considerable information can be obtained direct from the patterns, particularly if a homologous series of liquids is examined, has been shown by Stewart [7] for the primary normal alcohols and also for the fatty acids.

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[1] Debye and Scherrer, *Nachr. Gesell. Wiss.*, Göttingen, p. 16, 1916.

[2] Keesom and de Smedt, *Amsterdam Akad.*, 1922, **25**, 118; 1923, **26**, 112.

[3] Hewlett, *Physic. Rev.*, 1922, **20**, 688.

[4] Randall, *The Diffraction of X-rays and Electrons by Amorphous Solids, Liquids and Gases*, London, Chapman & Hall, 1934.

[5] Stewart, *Rev. Mod. Physics*, 1930, **2**, 116.

[6] Randall and Rooksby, *Trans. Faraday Soc.*, this volume, p. 109.

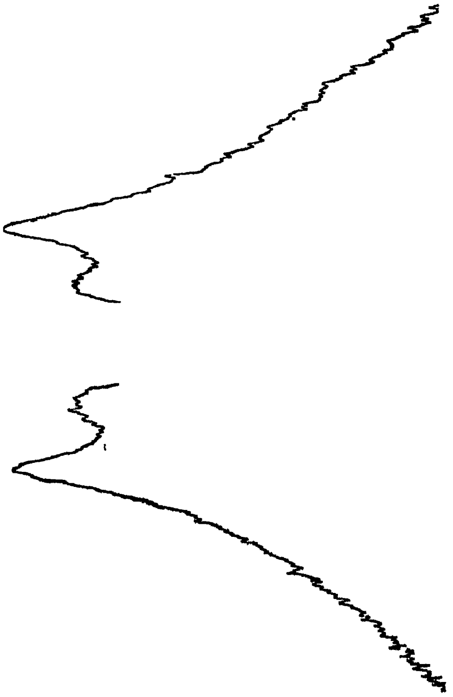

FIG. 1.—Microphotometer record of X-ray photograph of liquid rubidium: Cu-Kα radiation.

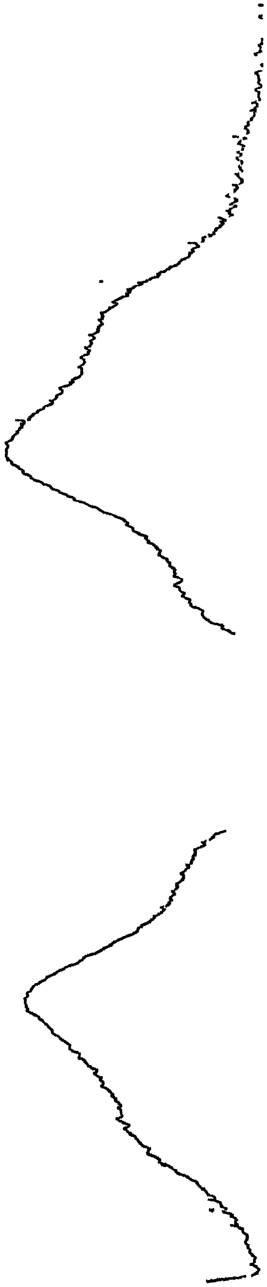

FIG. 2.—Microphotometer record of X-ray photograph of water: Cu-Kα radiation.

It has become increasingly clear however, during the last few years that really serious work on the interpretation of the X-ray diffraction patterns of liquids, depends more and more on the use of the Zernike-Prins [9] formula which expresses the intensity of coherent X-ray scattering as a sum of two expressions, the first of which is equivalent to the scattering if there were no interference between the waves scattered by different molecules; the second expression takes account of the distribution of scattering matter around any chosen molecule:

$$I_{2\theta}=Pnf^2\left[1+\int_0^\infty 4\pi r^2(g(r)-\rho)\,\frac{\sin sr}{sr}\,dr\right]. \quad (1)$$

Thus in (1) $I_{2\theta}$ represents the coherent scattering intensity of X-rays for a liquid of n molecules, each with a form-factor f. $4\pi r^2 g(r)dr$ represents the number of neighbours of any chosen molecule to be found at a distance r from it. ρ is the average density of the liquid in number of atoms (or molecules) per c.c.; $s = 4\pi \sin\theta/\lambda$ and P is the polarisation factor. Prins used this equation for his work on mercury.[10] The procedure (as used by Prins, Warren, and Bernal, for example) is essentially as follows. The observed diffraction pattern is obtained as a microphotometer record, the recorded deflections of which may readily be transformed into relative intensities. The relative intensities are then plotted against $\sin\theta/\lambda$ and corrected for the lack of polarisation in the incident beam and absorption in the specimen.[11]

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[7] Stewart, *Physic. Rev.*, 1928, 31, 174; 1928, 32, 153.

[8] Morrow, *ibid.*, 1928, 31, 10.

[9] Zernike and Prins, *Z. Physik*, 1927, 41, 184.

The procedure may now follow one of two courses: the more usual method up to the present time has been to obtain empirically a function $g(r)$ such that the theoretical curve obtained on integration of (1) is closely similar, in shape and position of maxima, to the experimental curve. This method has been used, for example, by Bernal and Fowler.[12] in their work on water, and has the advantage of giving a clear physical picture. Debye and Menke [13] have used the method of Fourier inversion to transfer a probability function W to the left-hand side of an equation somewhat similar to (1).

The Debye-Menke equation for intensity of scattering is, in fact,

$$I_{2\theta} = Pnf^2\left[1 - \frac{2\lambda^3}{d^3}\int_0 p(1 - W)\,\frac{\sin 2\pi ps}{s}\,dp\right] \quad . \quad . \quad (2)$$

where s here $= 2\sin\theta$ and $p = r/\lambda$.

W expresses the probability of finding atoms or molecules at any chosen value of r.

By Fourier inversion (2) transforms into

$$p(1 - W) = \frac{2d^3}{\lambda^3}\int_0^\infty s(1 - E)\sin 2\pi psds \quad . \quad . \quad (3)$$

where $$I_{2\theta} = Pnf^2E(s).$$

$E(s)$ can therefore be obtained from the experimental curve and the equation solved for W. This results in a general picture of scattering matter but, as so far presented, fails to give details of a kind most valuable.

I have found that equation (1) may be put in the much more useful form given below. The new expression is

$$\Sigma 4\pi r^2 E_r f_0 = \Sigma 4\pi r^2 E_0 f_0 + \frac{2r}{\pi}\int_0^\infty s\phi(s)\sin rsds \quad . \quad . \quad (4)$$

where $$\phi(s) = \frac{I/p_n - f^2}{f_e^2},$$

I being the observed intensity of diffraction,

$$4\pi r^2 E_r \mathrm{d}r = 4\pi r^2 g(r)\mathrm{d}rf/f_e g(n)$$

$g(r)$ being the same as in Prins's formula. $4\pi r^2 E_r \mathrm{d}r$ is therefore the effective number of electrons lying between radii r and $r + \mathrm{d}r$, and f_0 is written for f/f_e, where f_e is the average f per electron taken over the molecule, and $E_0 f_e/f = \rho$ where ρ has the same significance as in (1). The summation in (4) takes place over the whole molecule.

Equation (2) then gives the weighted radial distribution of scattering matter as determined (*a*) by the positions of the peaks, and (*b*) by the areas under the peaks of the $\Sigma 4\pi r^2 E_r f_0 - r$ curve. The equation is, in fact, put on an absolute basis in the derivation of $\phi(s)$, since the coherent scattering approximates to f^2 for large values of $\sin \theta/\lambda$. The areas under the peaks of the $\Sigma 4\pi r^2 E_r f_0 - r$ curve can then be used to give the number of neighbours of any particular ion, and this may of course be the co-ordination number.

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[10] Prins, *Physica*, 1926, 6, 315.

[11] Blake, *Rev. Mod. Physics*, 1933, 5, 169.

[12] Bernal and Fowler, *J. Chem. Physics*, 1933, 1, 515.

[13] Debye and Menke, *Physik. Z.*, 1930, 31, 797.

It is a matter of choice whether the method involved in equation (4) is adopted. The chief advantages of this over previous methods lie in the fact that it is to a close degree of approximation, absolute, and secondly, that it avoids somewhat doubtful assumptions about the distribution function, and the numerous laborious trials involved.

Recent work on the structure of liquids as determined by X-ray methods makes it clear that it is of little more than superficial value to give only the equivalent spacing of any band or bands which may exist, unless the photograph has been converted to an intensity scale and corrected for absorption. It is in fact the *shape* of the whole curve rather than isolated peak values which must be used in such calculations as have been indicated. Should such a method as that of absolute Fourier analysis come into general use it will be perfectly legitimate to speak of determination of structure in a liquid; for, in spite of thermal motions and migrations, the fundamental co-ordination groups, such as are suggested by analysis of crystals, exist without change, and it is likely that the method will be of some interest where the direction of bonds are in dispute. In the case of hydrogen peroxide, for example, it is hoped to settle the point as to whether the skew model of Penney and Sutherland fits in with the proposed arrangement of OH groups; in sulphuric acid it will be possible to compare the results on the SO_4 group with crystal analysis determinations of sulphates.

A considerable amount of experimental work has been carried out on solutions by Krishnamurti,[14] A. W. Meyer,[15] H. H. Meyer,[16] and Prins,[17] but little of a quantitative nature is really known, apart from the diffraction pictures themselves. The Fourier method should supply a means of determining or corroborating known values of the degree of hydration of various ions in solution. The inter-ionic distances so obtained should be of some interest and value, as it appears possible from work now proceeding that such " distances " can be determined, if not with the precision of crystal analysis, at least to 3 or 4 hundredths of an Ångström.

Although the present discussions are confined to liquids, it should be remembered, that, from the point of view of X-ray analysis, glasses fall into the same category; there is regularity of co-ordination but no large scale regularity or precision. It should now be possible to determine the interionic distances of cations and anions in some of the more unusual glasses, *i.e.*, in circumstances which are not commonly met in crystalline silicates, and for which empirical $g(r)$ curves are not readily suggested. In this respect, one might mention glasses containing ZnO or Al_2O_3, but considerably smaller amounts of SiO_2 than is usual, for example, in soda-lime-silica glasses.

Finally, one may say that the Fourier analysis method as here outlined may be of great value in studying the spatial configuration and types of bond in many organic liquids. Given adequate control of temperature, the process of melting could also be studied in a way that has not hitherto been possible, and this should be of particular interest where change of structure is known, from other evidence to occur.

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[14] Krishnamurti, *Indian J. Physics*, 1928, **2**, 500; 1929, **3**, 307; 1930, **5**, 489.
[15] A. W. Meyer, *Physic. Rev.*, 1931, **38**, 1083.
[16] H. H. Meyer, *Ann. Physik*, 1930, **5**, 701.
[17] J. A. Prins, *Nature*, 1929, **123**, 84.

THE IDENTITY OF STRUCTURE IN LIQUID LEAD AND BISMUTH.*

By J. T. Randall, M.Sc. and H. P. Rooksby, B.Sc. A.Inst.P.

Received, 12th *June*, 1936.

The present note gives an account of X-ray diffraction measurements on the liquids lead and bismuth. Some earlier measurements have already been recorded [1] by one of us, and it was clear that while liquid lead remained essentially close-packed, liquid bismuth showed considerable structural change on melting. Lead and bismuth occupy contiguous positions in the ninth row of the periodic table and Professor Mott, as a result of his work on the quantum theory of metals, has suggested to us that there should be strong structural similarity between the liquids. Solid bismuth is hexagonal in structure; [2] a notable feature is the occurrence of the (111) planes in alternate pairs of strong and weak attraction. Bismuth in common with antimony and gallium has a higher conductivity in the liquid than in the solid phase. The fact that the high diamagnetism of antimony and bismuth disappears on melting suggests that the liquids are close-packed. Professor Mott interprets this in terms of the "Brillouin zones" and considers that the zone characteristic of solid bismuth, which contains five electronic states per atom, disappears on melting. This leads to the conclusion that liquid bismuth would have a normal resistance comparable with that of lead. This has been observed by Pietenpol and Miley.[3]

The X-ray diffraction patterns of the liquids were obtained from specimens enclosed in evacuated capillary tubes of exceedingly thin glass of low mass absorption coefficient. A small amount of metal was distilled to an appropriate position on the tube and the temperature during the period of exposure was maintained just above the melting-point by an external heating spiral. The high mass absorption coefficient of lead and bismuth for X-rays, made it essential to obtain and maintain a very thin film of metal in the glass tube. The metals showed a tendency to form into small globules of too great a thickness and several attempts were made before satisfactory films were produced. Cu-Kα radiation was used and the diffracted rays were photographed on flat films which were subsequently microphotometred on a Moll instrument. On the microphotometer record for liquid lead, there was included a record of the solid to give a spacing check, and a similar procedure was adopted for bismuth.

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* (Communication No. 201 from the Staff of the Research Laboratories of The General Electric Company Limited, Wembley, England.)

[1] J. T. Randall, *The Diffraction of X-rays and Electrons by Amorphous Solids, Liquids, and Gases*, London, Chapman and Hall, 1934, pp. 133-4.

[2] R. W. James, *Phil. Mag.*, 1921, **42**, 193; O. Hassel and H. Mark, *Z. Physik*, 1924, **23**, 269.

[3] Pietenpol and Miley, *Physic. Rev.*, 1929, **34**, 1588.

Both liquid lead and liquid bismuth give rise to a single diffraction band. The close-packed nature of liquid lead has already been referred to [1] and it is clear from the present results that the patterns for liquid lead and liquid bismuth are identical: the "spacings" calculated on the assumption that the Bragg law applies are: -

Liquid Lead	2·95 Å.U.
Liquid Bismuth	2·95 Å.U.

This exact agreement is probably fortuitous; it emphasises the absence of any appreciable structural difference between the two liquids. In the preliminary work referred to, the "spacings" were given as 2·90 Å.U. for lead and 2·94 Å.U. for bismuth; these values were the result of direct measurements on the negatives and are not so accurate as the new values taken from the microphotometer records.

It is clear that the measurements of electrical resistance on these liquids are in accord with the present structure determination and the quantum theory of metals.

SOME NEW RESULTS AND GENERAL INTERPRETATION OF DIFFRACTION BY AMORPHOUS SUBSTANCES.

By Professor J. A. Prins (*Wageningen, Holland*).

Received 22nd July, 1936.

New Results.—X-ray reflection photographs from free surfaces have been obtained by the author for some molten substances. ***Wood's metal***, ***tin*** and ***bismuth*** gave liquid patterns more or less resembling that of mercury. Even in an atmosphere of argon or carbon dioxide, oxidation was, however, not altogether eliminated, eventual oxide being clearly either amorphous or crystalline oriented. With *selenium* this difficulty was less disturbing, as the oxide is volatile. It was found that the diagram of molten selenium did not appreciably depend on temperature, and was identical with the one obtained from a preparation quenched by dropping it into water. In the case of sulphur it was necessary to cover the liquid with a thin aluminium foil to avoid burning. This technique gives the additional advantage of reference lines. On raising the temperature from 140-350° *no* appreciable change of spacing was found.[1]

TABLE I. -Spacing in A corresponding to Maxima of Diffraction

Liquid.	d_1.	d_2.	d_3.	Remarks.
Wood's alloy . .	3·14	1·56	(1·06)	No oxide.
Sn	2·83	—	—	Oxide ?
Bi	3·18	—	—	Vitreous [2] Bi_2O_3 ?
Se	3·38	1·79	1·15	No oxide.
S	3·43	—	—	Fluctuations $< 0·15$.

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[1] See A. H. Blatchford, *Proc. physic. Soc. London*, 1933, **45**, 493.

[2] J. T. Randall, London, 1934, The diffraction, etc., p. 177.

Liquid *alcohols* and *fatty acids* are known [3] to show a " long spacing " increasing with chain length. This phenomenon is not found with paraffins,[3] alkyl iodides or bromides,[4] esters [5] and not even with thio-alcohols, as the author has recently found.[6] For this reason it cannot be attributed to the general long chain character of the molecules. The author suggests that it is due to the polarity of the end groups (which is known to decrease strongly when sulphur is substituted for oxygen). In the case of the acids and alcohols the *strongly* polar end groups " are not soluble in the aliphatic bulk of the substance " and so cluster together; this clustering presumably induces a more or less layer-like structure, which is presumably *not* present in the case of the other, less polar, long chain liquids.

Solutions of heavy polyvalent ions show a " spacing " increasing with dilution.[7] This proves the existence of a kind of liquid arrangement of the solute particles, which the author has called "superarrangement." With lighter solutes the same effect is present and may even be discovered in previous work of other authors.[8] The interpretation is, however, not so cogent in this case.

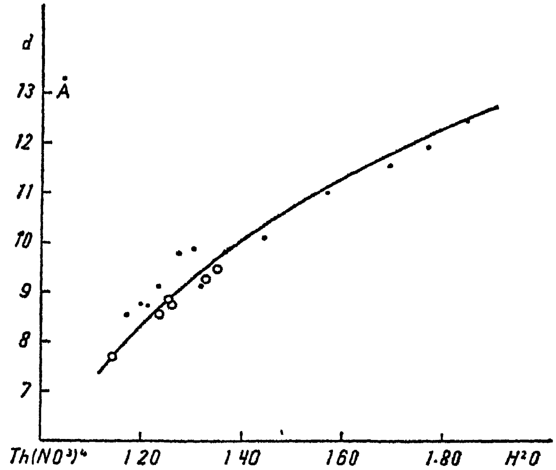

Fig. 1.—Variation of Spacing in Thorium Nitrate Solutions with Molal Proportion $Th(NO_3)_4 : H_2O$.[9]

● Measurements in wet atmosphere.

○ Measurements in dry atmosphere.

— Theoretical curve : $d = 1{\cdot}08$ (molal volume) $^{1/3}$.

Amorphous antimony is to be considered as a glassy substance.[10] It may be prepared electrolytically as " explosive antimony " or in a purer state, in *thin* layers, by evaporation at a high vacuum. The diffraction patterns of amorphous antimony prepared in these two ways are identical.[11] Incidentally, the appearance and growth of bluish opaque spots in a thin brownish and less opaque layer of antimony [12] has been studied by the author using electron diffraction and simultaneous visual observation. The results leave no doubt that the " brown " state is amorphous and the " blue " one crystalline oriented. Spontaneous crystallisation of thin amorphous layers at room-temperature is always accompanied by orientation of the trigonal axis normal to the surface of the film. It was found possible, however, to produce crystalline *non*-oriented layers from amorphous films by heating them quickly to about 120° C.

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[3] G. W. Stewart and R. M. Morrow, *Physic. Rev.*, 1927, **30**, 232.

[4] J. A. Prins, *Z. Physik*, 1929, **56**, 617.

[5] J. A. Prins and R. Fonteyne, *Physica*, 1935, **2**, 573.

[6] J. A. Prins, *Nederl. Tydschr. v. Natuurk*, 1936, **3**, 47.

[7] J. A. Prins, *J. chem. Physic*, 1935, **3**, 72.

[8] Shiba and Watanabe, *Sc. Rep. Inst. Phys. Chem. Res. Japan*, 1929, **10**, 187. W. Good, *Helv. phys. Acta*, **3**, 205.

[9] J. A. Prins and R. Fonteyne, *Physica*, 1935, **2**, 1016.

[10] G. Tammann and W. Müller, *Z. anorg. allg. Chemie*, 1937, **221**, 109.

[11] J. A. Prins, *Nature*, 1933, **131**, 760 and 1935, **136**, 299.

[12] H. Murmann, *Z. Physik*, 1929, **54**, 754.

Interpretation of Amorphous Diagrams.—Zernike and the author have shown that the only result which can be derived from the experimental pattern is the distribution law for the intermolecular distance.[13] This applies to any isotropic substance, *e.g.* even microcrystalline powders.[14] A superficial inspection of the pattern is not sufficient to form a conclusion whether the distribution in question has large fluctuations or not, in other words whether temporary "*groups*" are formed to any extent or not. Only quantitative measurement of the absolute scattering intensity at small angles can settle this controversial point.[15] From a theoretical point of view it is to be expected that only small fluctuations in accordance with the small macroscopical compressibility exist, at least in ordinary liquids. With glasses the case is quite different. Here the degree of organisation *may* be appreciably different in neighbouring small regions. Indeed, an increasing amount of experimental material indicates that in this way a gradual transition from the amorphous to the crystalline state may occur. This does not, however, apply to ordinary liquids and is only made possible in glasses by their high viscosity, which allows deviation from thermodynamical equilibrium.[16]

A *chaotic state* of aggregation "more amorphous than the liquid state" has more than once been revealed by the diffraction method (no clear minimum at small angles). This state seems to occur mostly when atoms are brought together at a temperature very far below the melting-point of the corresponding substance. Moreover, impurities seem to favour the occurrence of the chaotic state.

*GENERAL DISCUSSION.**

Dr. E. Bauer (*Paris*) said: Experiments carried out with the Raman effect in the Laboratory of Collège de France, yielded results with conclusions somewhat similar to those of Professor Prins, and give us some precise information on the structure of solutions.:

(1) with concentrated solution of Mg[17], Th (Al ?)(Cu ?) we obtained well defined bands of ion hydrates; these show a stable association between water molecules and ions of sufficiently small size and large valency. We may admit as a rough picture that the hydrate of the ions in saturated solution of $Th(NO^3)^4$ are in contact; this picture explains easily Prins' experimental results. In dilute solutions we must rather consider the electrostatic equilibrium between water molecules and ions.

(2) In a study of the doubling due to the cation of the 717-743 band of the NO^3 ion in solutions of variable concentration of $Ca(NO_3)_2$ we observed[18] that the distance between the two components increases with concentra-

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[13] F. Zernike and J. A. Prins, *Z. Physik*, 1927, **41**, 184. See also P. Debye and H. Menke, *Physik. Z.*, 1930, **31**, 797.

[14] B. E. Warren and N. Gingrich, *Physic. Rev.*, 1934, **46**, 368.

[15] A measurement by P. Krihnamurti favours small fluctuations (no groups), but no other absolute measurements seem to have been made.

[16] F. Simon, *Z. anorg. allg. Chemie*, 1931, **203**, 219.

* On preceding three papers.

[17] Silveira and Bauer, *Comptes rendus*, 1932, **195**, 415.

[18] Bauer, Magat and Silveira, *ibid.*, 1933, **197**, 313.

tion, while their half-width becomes smaller; particularly in saturated solutions the two lines are very narrow. It seems that the distribution of anions and cations in those solutions is not random, but that their relative distance varies closely around a certain mean value.

Dr. M. Magat (*Paris*) said: Can you derive conclusions from your experiments as to the sub-structure in the neighbourhood of anions?

Professor J. A. Prins (*Wageningen*) said: Regarding the remark (2) of Dr. Bauer and that of Dr. Magat, it is of interest that X-ray diffraction shows a super-arrangement in the case of some anions, *e.g.*, (WO_4) and ($PtCl_6$). The super-arrangements of the ions themselves should, however, not be confused with the arrangement of the water molecules surrounding an ion. For "sub-arrangement" see remark on Stewart's paper.

Dr. M. Magat (*Paris*) said: The interaction between anions and water, although less important than that between cations and water must not be neglected. Thus we found in the case of the intramolecular bands of water[19] that the intensity of one of them (1650 cm^{-1}) depends on the cation (it is very strong in solutions of Th and Ca), while the relative intensity and distance between the two others (3200 and 3400 cm^{-1}) vary only with the anions.

Professor F. G. Donnan (*London*) said: I should like to ask Professor Prins whether aqueous solutions containing the large ionic micelles of long chain paraffin salts[20] would show special effects when examined by X-ray diffraction methods.

Mr. E. A. Guggenheim (*London*) suggested that the effect found with thorium ions might be detectable with complex anions of high valency having a heavy central atom. The number of known anions of this type is considerable, and some of these should be sufficiently stable and well defined for the purpose. The salt $K_4Os(CN)_6$ might be the most suitable.

Professor J. H. Hildebrand (*Berkeley, Cal.*) said: The case of benzene and cyclohexane, to which reference has been made in the discussion, appears to me a most unlikely one for the occurrence of clusters, since the deviation of the vapour pressures from Raoult's law is rather small, in harmony with their moderate difference in internal pressure. A system such as silicon chloride and stannic iodide, which form two liquid phases below 135°, would be a much better one to investigate by means of X-rays.

Dr. R. J. W. Le Fèvre (*London*) said: A discovery of certain contrasts between corresponding oxygen- and sulphur-containing organic compounds cannot alone be held to constitute a criticism of Stewart's hypothesis of a cybotactic condition in liquids, in view of the considerable changes of molecular shape which must follow the replacement of an element of 0·7Å radius (O) by one of 1·06 Å (S), the possible alteration of valency angles within the molecule consequent upon such substitution, and the certain difference (to be expected from the non-identity of the atomic refractions of O and S) in the anisotropy of polarisability of the molecule which this interchange would create.

Dr. J. D. Bernal (*Cambridge*) said: I am particularly interested in the points that Dr. Prins has raised about the existence of crystalline or pseudo crystalline groups in glasses. It seems to me that in an ideal quickly chilled glass in bulk, regular groups of molecules should not be expected, but that in an aged or semi-annealed glass such groups may well exist long before actual crystals can be detected by visual methods. In any given small region of the glass there may even be some semblance of long range order in the Bragg and Williams sense, mixed with considerable disorder. On heating, each of these small regions would become a regular crystal. The same effect could, however, be achieved in another way. On powdering a glass a certain freedom of re-arrangement is regained, and each small fragment may become a single crystal. This will be easier the smaller the fragment. The observations on the sharpness of the X-ray crystal pattern in very fine crushed silica glass supports this view. I have myself observed in the case of a complex organic glass which had been coarsely crushed and allowed to stand for some months, that each fragment while still glassy in appearance had become birefringent, and was, in fact, as shown by X-rays, a single crystal still mixed, however, with varying amounts of glassy material.

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[19] Magat, *Ann. Physique*, 1936.

[20] See, for example, "Aqueous Solutions of Paraffin Chain Salts" by G. S. Hartley; No. 387 of *Actualités Scientifiques et industrielles*, published by Hermann & Cie, Paris.

A clear distinction ought to be made in the case of solutions between two kinds of arrangements, the super arrangements of ions relative to one another in the liquid studied by Prins and giving effects varying with the concentration, and the other arrangement which is a variety of Prins' sub-arrangements of solvent molecules round a particular ion. This is also detectable in certain cases by X-rays but the effect is independent of the concentration. On the other hand, it is this effect that is observed by means of Raman and infra-red measurements where we are dealing with the vibrations with the solvent molecules against the ions.

M. M. Mathieu (*Paris*) said : Such a " chaotic " state as is mentioned at the end of Professor Prins's paper is very often found when hydrated salts are dehydrated. For a well-defined water vapour pressure, and at temperatures between the dissociation temperature and the rather indefinite temperature of crystallisation of the dehydrated salt, only a general X-ray scattering is observed. Some experiments on the sulphates of the metals of the magnesia group are now being carried on in order to test further this idea of a " chaotic " state.

Professor J. A. Prins (*Wageningen*), in reply, said : Most of the remarks made will lead to more experimental work. Some work has, indeed, already been done by various investigators on the subject mentioned by Professor Donnan.

RAMAN SPECTRA AND THE CONSTITUTION OF LIQUIDS.

By Michel Magat.

Received in French, 24th August, 1936.

It is known that the interaction of neighbouring molecules affects their spectra in two different ways, *viz.* by a variation of the frequencies of the individual molecules and by the appearance of new, *intermolecular*, frequencies. These two effects, studied by Errera and his colleagues in the infra-red, may also, and frequently more readily, be observed in the Raman spectra. This paper records briefly our results and the conclusions drawn therefrom as to the structure of liquids and particularly of water.

Conditions under which Intermolecular Bands appear in Raman Spectra.

Two conditions must be fulfilled :—

(1) The breadth of a spectral band, in case of emission by *several* analogous systems is inversely proportionate[1] to (*a*) the life period of the system in the two states of vibration and (*b*) the identity of the systems. For example, a ray or band of finite breadth will only be emitted if the life period of the complex to which it is due is large

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[1] This condition should also be fulfilled for the appearance of distant bands in the infra-red.

compared with the emitted frequency; that two or more molecules in quasi-elastic collision (*i.e.* infinitely separated after approach to the barrier of repulsion) cannot give rise to a band of definite frequency but only to a continuous spectrum. On the other hand, if the complexes differ materially from one another, as by intermolecular distance or force of interaction, a whole series of frequencies will be emitted, giving, in the limit, a continuous spectrum. For this reason the " classic " theory of liquids, which considers them as gases compressed to a state of disorder, predicts a continuous Raman spectrum for liquids.

(2) The intensity of the Raman ray depends on the factor $\partial\alpha_{ik}/\partial g_k$ where α_{ik} is a component of the tendency to polarise and g_k the co-ordinate which varies during the oscillation, *i.e.* the intermolecular distance. For a Raman band to appear, then, the electronic polarisibility must vary with the intermolecular distance, *i.e.* with the density. In other words, the bands only appear in cases when the Clausius-Mosotti law is not strictly valid; this law applies, *e.g.* to nitrogen, so that intermolecular Raman bands should not be expected for solid or liquid nitrogen.

An idea of the probable intensity of intermolecular Raman bands of a liquid may be obtained by comparing the electronic polarisibility α in the gas and in the liquid or solid.[2] Table I. shows that, in the case of water, intense bands can be expected.

The frequency of these bands can easily be ascertained. If the attractive force due to the interaction of the dipoles $\mu \sim 1$ D, and if the dipole distance is of the order 3 Å. and the mass of the order 50 g. mol., we find $\nu \sim 140$ cm.$^{-1}$.

TABLE I.

Substance.	State.	t°C.	Density.	$\frac{4\pi}{3}N\alpha$
H_2	gas	0	$8·987 \times 10^{-3}$	
	liquid	− 252·8	$7·097 \times 10^{-3}$	
N_2	gas	0	$1·2506 \times 10^{-3}$	4·446
	liquid	195·8	0·8075	4·421
CCl_4	gas	20°		26·60
	liquid	20°	1·594	26·48
H_2O	gas	150°		3·766
	liquid	0°	0·99987	3·714
	liquid	98°	0·95981	3·707

Experimental Results.

In the Raman spectrum of water, Bolla[3] and the author[4] independently, found weak frequencies which the author attributed to intermolecular bands.[5] Later, Gross and colleagues[6] studied the intermolecular bands of solid benzene and naphthalene, etc.; after melting the bands broaden considerably so as to represent the maxima of the " wings " of the exciting ray but their position is practically the same. Finally, Ananthakrishnan[7] and the author[8] studied the bands of heavy water. We may mention that Briegleb and Lauppe[9] found intermolecular bands due to the formation of different molecular complexes, but this work as well as that of Brodsky[10] is beyond the scope of this paper. Table II. summarises the intermolecular bands actually known, indicating (where known) their intensity and their polarisation.

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[2] Or by comparing the position of the maxima of the ultra-violet absorption in the two states.

[3] G. Bolla, *Nuovo Cimeoto,* 1933, **10,** 101.

[4] M. Magat, *C.R.,* 1933, **196,** 1981; *J. Physique,* 1934, **5,** 347.

[5] Great care must be taken when working in this region with the mercury arc, since the arc itself has intense rays with abundant neighbouring cloudy and weak rays which may easily be confused with Raman spectra. The intensity of these clouds which we have catalogued (*J. Physique,* 1934, **5,** 347) probably depends on the arc conditions.

[6] Gross and Vuks, *Nature,* 1935, **135,** 100, 998; *J. Physique,* 1936, **7.**

TABLE II *

Substance.	Intermolecular Frequencies.											
	$\Delta\nu$	Intensity. M.	ρ	$\Delta\nu$	Intensity. M.	ρ	$\Delta\nu$	Intensity. M.	ρ	$\Delta\nu$	Intensity. M.	ρ
C_6H_6	—	—	—	—	—		62	-	—	104	-	*P*
$pC_6H_4Br_2$	20	—	*P*	38	—	*P*	—	—	—	93		*P*
$C_{10}H_8$	45	—	*P*	73	-	*P*	109	—	*P*	124		*P*
$(C_6H_5)_2O$	22	*F*	*P*	38	*f*	*P*	67	*f*	*P*	104	*F*	*P*
H_2O	60	*f*	–	176	*m*	*D*	500	*f*	*P*	700	*f*	*P*
D_2O	—	—	—	170	*m*	-	350	*f*	–	500	*ff*	-

* Frequency in cm.$^{-1}$ Intensity : *F* intense, *m* mean, *f* weak. Polarisation : *P* polarised, *D* depolarised.

Discussion.

The " classic " theory, which excludes distinct intermolecular bands, must then be abandoned. We must admit that liquids have a structure, in conformity with the conclusions of Stewart and Debye from X-ray diffraction study, and of Briegleb[11] from study of the electro-optic effect.

However, as Bernal[12] has shown, the Raman bands also make it possible to distinguish between the different theories adduced to explain X-ray diffraction by liquids, *viz.* that of the " micro-crystalline " and that of the " quasi-crystalline " structure of liquids. Whilst the former presumes the existence of minute " perfectly crystalline " agglomerates floating in a liquid atmosphere of " non-oriented " molecules, the latter supposes a *correlation* between the mutual orientations and distances of neighbouring molecules, which spreads over many molecules and becomes increasingly weaker as the distance increases. If the whole of a liquid is at room temperature, either perfect crystals nor groups of entirely free molecules are found.

If relatively many particles go to make up a " microcrystal " the position and breadth of the intermolecular bands should be the same in the solid and in the liquid—only their intensity should decrease on melting. The " quasi-crystalline " hypothesis, presuming deformation of the very structure of the layer immediately surrounding a molecule, does not lead one to expect any sensible weakening, but rather an increase in the breadth of the band and a slight displacement towards the weaker frequencies, in comparison with the band of the solid; this was observed by Gross and Vuks.[6] The "micro-crystalline" hypothesis necessarily implies in this case the further assumption that only very few molecules are present in each agglomerate. But, if we are to explain the relatively large intensity of the intermolecular bands, we must presuppose the existence of a large number of micro-crystals, which, in the limit, is the same thing as the "quasi-crystalline" hypothesis. The latter, therefore, seems to be the correct one.

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[7] A. R. Ananthakrishnan, *Proc. Ind. Acad, Sciences*, 1935, **2**, 291 ; 1936, **3**, 201.

[8] E. Bauer and M. Magat, *Comptes rendus*, 1935, **201**, 667.

[9] G. Briegleb and W. Lauppe, *Z. physikal. Chemie, B*, 1935, **28**, 154.

[10] A. E. Brodsky, A. M. Sack and S. F. Besugli, *Z. Physik, Sow. U.*, 1934, **5**, 146 ; *J. Chem. Physics*, 1935, **3**, 449 ; *J. physitcheskoi chimii*, 1936, **7**, 859.

[11] G. Briegleb, *Z. physikal. Chemie, B*, 1931, **14**, 97 ; 1932, **16**, 249.

[12] Bernal, Gaster Conference of Soc. de Physique, Paris, 1935.

The Raman Spectra of Water.

The bands of water have so far been the most thoroughly investigated and we can now seek to ascertain their origin. Their fundamental frequencies are 60, 176 (152-225), 500 and 700 cm.$^{-1}$. We can attempt to calculate these frequencies from a model of the molecule and a model of the possible modes of vibration.

Bernal and Fowler[13] have given a reasonable model of the distribution of charges in a molecule of water, which has the great advantage that it does not characterise molecules by their electric dipoles only, but takes into account also the approximate distribution of the charges within the molecule. Fig. 1 shows such a model slightly modified in the light of later work.[14]

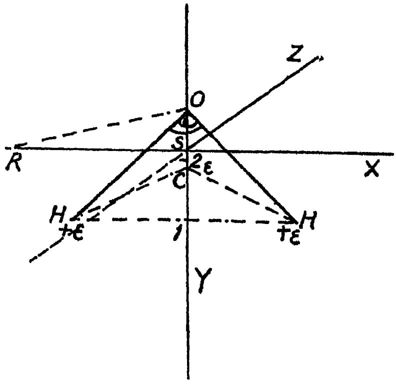
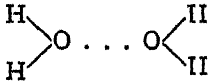
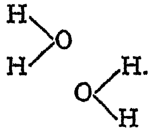
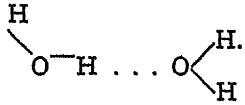


FIG. 1.

S = centre of gravity of masses.
C = centre of gravity of negative charges.
OH = 0·970 Å. H—H = 1·539 Å.
O—C = 0·16 Å. ∢ HOH = 105°.
$\epsilon = 0{\cdot}45e = 2{\cdot}14 \times 10^{-10}$ u.e.s.
$OR = \frac{O-O}{2} = 1{\cdot}36$ Å.

We can now figure the energy of interaction of two atoms for different orientations.[15] Doing this for a series of characteristic positions, in particular of the dipoles, we find for all of them either a repulsion:  or a weak attraction:  The only position giving a noteworthy attraction is  If we seek to continue this structure in space we find, the one corresponding to the absolute minimum of energy. It is the quartz structure, proposed by Bernal and Fowler[13] to explain the X-ray diffraction of water. We can also find the energy of activation necessary for a molecule to turn freely round each of its axes in the field of four neighbouring molecules. Fig. 2 shows this energy per gm. mol. as a function of the angle formed with the direction of the minimum position. The difference between the absolute maximum and minimum represents the total activation energy. These figures are very high and certainly higher than the energy really required, since the rotation of a molecule decreases the rotational activation energy of its neighbours (Fig. 2). One fact, however, is certain: except the rotation around the y axis there is practically no free rotation in water of room temperature, as is shown by Debye, Bernal, and Fowler by quite different methods. We can therefore evaluate the frequencies of "libration" (orientation oscillation) and of vibration properly so-called. For libration around the z axis we find[16] 570 cm.$^{-1}$ and for the contraction of the tetrahedron of 5 molecules 180-280 cm.$^{-1}$ (180 considering the molecule vibrating peripherally and 280 counting it as the central molecule). This agrees well with experiment (500 and 152-225). The band 176 (152-225) cm.$^{-1}$, then, seems to be due to vibration, and the bands 60, 500 and 700 cm.$^{-1}$ due to oscillation around the axes y, z and x respectively.

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[13] Bernal and Fowler, *J. Chem. Physics*, 1933, **1**, 515.
[14] By reasonably varying the model the same results are reached.
[15] M. Magat, *Ann. Physique*, 1936, **6**, (11), 108.

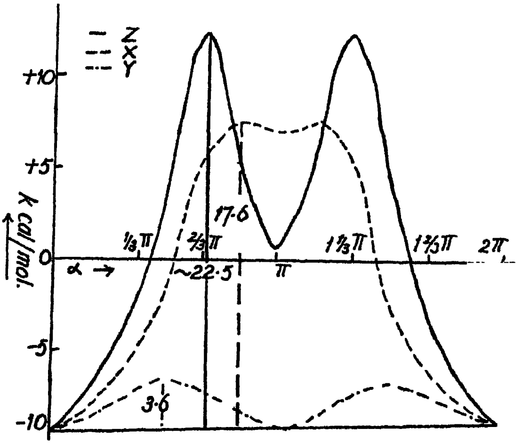

FIG. 2.

Control with the Raman Spectra of D_2O.

By studying the intermolecular bands of D_2O we readily see that the increase of the vibrating mass due to substitution of hydrogen by deuterium only slightly influences the vibration frequency: $\sqrt{18}/\sqrt{20}$. The frequency 176 cm.$^{-1}$ in fact[17] becomes 170. On the other hand the bands corresponding to "libration" should be considerably displaced. The ratio of frequencies in D_2O and H_2O should be equal to a first approximation[18] to the ratio of the moments of inertia, *i.e.* $\sqrt{1}/\sqrt{2}$. Now $350/500 = 1/1{\cdot}43$ and $500/700 = 1/1{\cdot}40$, thus confirming the above analysis of the intermolecular bands.

There are difficulties still to overcome however. The band 176 cm.$^{-1}$ (being a symmetrical vibration band) should not appear in the infra-red, but it does.[19] On the other hand this symmetrical vibration band should be strongly polarised whilst its degree of depolarisation is in fact 6/7

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[16] See also Bernal and Tamm.

[17] Cartwright, *Nature*, 1935, 136, 181; see also Table II.

[18] On second approximation this ratio is modified by a variation in the retractive force due to a displacement of the centre of gravity.

[19] C. N. Cartwright, *Nature*, 1935, 135, 872.

(Ananthakrishnan). These difficulties arise, however, only in the "micro-crystalline" theory which, as we have seen, is inexact; in the "quasi-crystalline" theory total symmetry of vibration is *a priori* impossible, so that any objections so arising are invalid.[19a]

Temperature Effect.

It will be interesting to study the temperature effect. From many experiments we find that the intensity of the 500 and 700 cm.$^{-1}$ bands decreases much more rapidly with temperature than that of 176 cm.$^{-1}$, particularly at about 40° C. On searching the literature we find that *all* properties of water are anomalous at this temperature; for example, the compressibility (Amagat) (Fig. 3) and specific heat (Fig. 4) [20]. We may also mention the disappearance of the second maximum in Stewart's X-ray diffraction figures and the thermal expansion of water under pressure.[21] Analysing these curves more closely we see that the variations at about 40° C. correspond apparently to a change of phase of the third order (discontinuities in the second energy derivatives); this probably corresponds to the appearance of a rotation around the y axis.

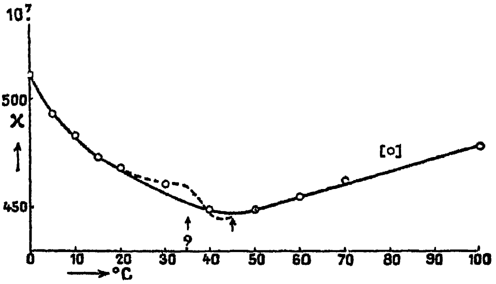

Fig. 3.

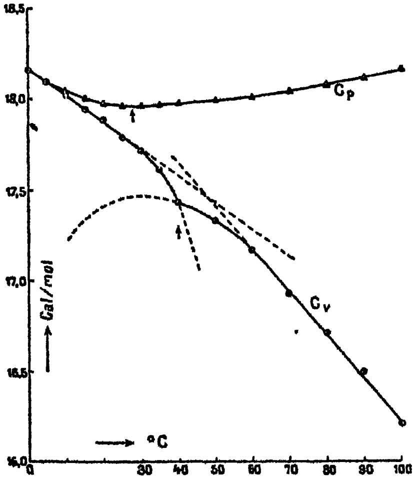

Fig. 4.

Intramolecular Frequencies.

The investigation of these should, as we have said, give interesting results. We emphasise that the Raman effect as a method is preferable to infra-red spectroscopy, because we can thus study variations in the fundamental frequencies whilst infra-red spectroscopy (very difficult in this region) often necessitates the study of higher harmonics only where the different effects lead to complications by their superimposition.

We have studied the intensities and the positions of the intramolecular Raman bands of water above and below 40° C. This temperature appears to play an important part; the ratio of intensity of the 3200 and 3400 cm.$^{-1}$ bands appears to remain approximately constant between 12° and 40° and to decrease noticeably between 40° and 70°.

[19a] C. Venkateswaran, *Proc. Ind. Acad. Sc.*, 1936, 4, 345, 414, found that intermolecular vibration bands of S and P are also fully depolarised.

[20] M. Magat, *J. Physique*, 1935, 6, 179.

[21] Bridgman, *The Physics of High Pressure*, p. 145.

On the other hand, the distance between the two bands decreases rapidly from 12° to 40° and then remains constant. The intensity of the 3600 cm.$^{-1}$ band, which is not shown on our figures at room temperature, becomes noticeable and clearly increases at higher temperatures. E. Ganz [22] observed analogous effects in the infra-red on the 0·77 μ band.

Summary.

The Raman effect leads us to favour unambiguously for the structure of liquids, the quasi-crystalline hypothesis. On the other hand it enables us to decide the structure of the liquids to be adopted in particular cases and to verify the results of the X-ray investigation. It finally shows that liquids, as well as solids, may possess points (or more correctly intervals) of transformation bound up with the appearance of free rotation.

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[22] E. Ganz, *Ann. Physik*, 1936, **26**, 331.

STRUCTURE OF LIQUIDS STUDIED IN THE INFRA-RED.

BY J. ERRERA (*Brussels*).

Received in French 31st July.

Among the conditions limiting the conception of the viscosity of a liquid are the dimensions (which have to be large in regard to molecular diameters) in which the phenomenon is considered and the time of observation (which should be large relatively to the time between molecular collisions).

In earlier work,[1] relating to the first condition, we dealt with the lower limit of the capillary diameter for which Poiseuille's law is valid in the case of pure liquids, *e.g.*, when using as viscometer membranes of cellulose or of cellulose derivatives having a mean pore diameter of the order of 26mμ. We have compared these results with those of Collander [2] who used semi-permeable molecular membranes for which the rate of passage was a function of the molecular diameter.

As to the second condition, the work which confirmed Debye's theory of anomalous dipolar dispersion [3] showed that for hertzian frequencies (ν of the order of 10^8) the dispersion phenomenon of the dielectric constants (d.c.) and the accompanying absorption seem to accord with the conception of macroscopic viscosity, so that the law of Poiseuille applies. May it not be that on increasing the frequency we shall find deviations from this conception, from which we can draw conclusions as to liquid structure? To this end we observed the anomalous dispersion and the absorption in the far infra-red.

The influence of an electric field on a polar molecule in the liquid state corresponds to the orientation, in a viscous medium, of a body carrying an electric moment. If the field is suppressed the molecules do not assume random distribution until after a certain time, which is so much the greater as the force of friction is larger and the temperature lower. Debye defines thus a relaxation time, τ, *i.e.*, the orienting action of the field τ seconds after its interruption has fallen to the value $1/e$. If η is the macroscopic viscosity and if we imagine spherical molecules of radius a and that the laws of macroscopic viscosity are valid, we have the relation:

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[1] J. Duclaux and J. Errera, *Rev. Gen. Coll.*, 1924, **2**, 130, and 1925, **3**, 97; *Koll. Z.*, 1926, **38**, 54.

[2] Collander, *Koll. Chem. Beih.*, 1924, **19**, 72.

[3] P. Debye, *Ber. deutsch. physik. Ges.*, 1913, **15**, 777.

$$\tau = \frac{4\pi\eta a^3}{kT}$$

where k is the Boltzmann constant and T the absolute temperature.

If now the frequency of the field is increased so as to approach that of $1/\tau$ the dipoles can no longer be oriented. Debye gave the theory which involves an anomalous dispersion of the d.c. ϵ (equivalent to the square of the refractive index n measured at the same frequency, $\epsilon = n^2$). These values decrease as the frequency increases. Dispersion is accompanied by an absorption of energy, since the orientation and the directive field are out of phase. From this theory we can calculate τ and from that a, starting either from values of the d.c. or the index or from those of the absorption.

Studies of dispersion and of absorption so far made in the hertzian region have been carried out at frequencies (ν about 10^7 to 10^8) less than $1/\tau$. For normal liquids, $\nu_0 = 1/\tau$ is of the order of 10^{10} to 10^{11} (0·3 to 3 cm.$^{-1}$). The d.c. has been determined [4] at different frequencies either by capacity measurements or by determining the wave-length of the electro-magnetic wave in the medium, and from these values τ and a have been calculated. The absorption has been determined either by directly measuring the amount of heat released or by measuring the apparent conductivity, which served also for calculating τ and a by Debye's theory.

These measurements were made on pure polar liquids, preferably, in dilute solution in a non-polar liquid. Since a so determined agrees generally with that obtained by other physical methods, it appears to follow that, for ν less than $1/\tau$, macroscopic viscosity still plays its part, even for rotational movements of the molecule.

The measurements which we now report were carried out in the far infra-red region between 52μ ($\nu = 192$ cm.$^{-1}$ or 6×10^{12}) and 152 μ ($\nu = 66$ cm.$^{-1}$ or 2×10^{12}), *i.e.*, ν greater than $1/\tau$. The refractive indices, n, were determined by measuring the reflective power and the absorption by transmission measurements, which give directly the extinction coefficients

($\kappa = 4\pi n \alpha \nu$, ν in cm.$^{-1}$).

The values are taken either from our earlier paper with C. H. Cartwright,[5] or from more recent measurements made in our laboratory by L. Hauss and A. Prigogin.

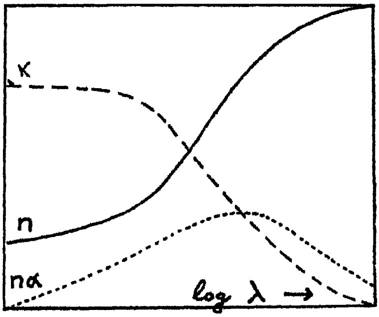

Fig. 1.

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[4] See, for bibliography up to 1934, P. Debye and H. Sack, *Hand. Radiol. VI.*, 1934, **2**, 69, and, amongst more recent work, P. Girard and P. Abadie, *J. Physique*, 1935, **6**, 295; 1936, **7**, 211; P. Debye, *Trans. Faraday Soc.*, 1934, **30**, 679; J. Henrion and W. van der Grinten, 2 *Congrès Nat. des Sciences*, Bruxelles, 1935, p. 341. J. Henrion, *Bull. Soc. Sc. Liège*, 1936, p. 22.

[5] *Acta Physico-Chem. U.R.S.S.*, 1935, **3**, 649, and *Proc. Roy. Soc.*, *A*, 1936, **154**, 138. See these papers also for the methods of measurement, calculation, etc.

Fig. 1 shows diagramatically the theoretical shape, according to Debye's formula, of variations of n, of the absorption coefficient $n\alpha$ and of κ in the region of dipolar dispersion for liquids; for non-polar bodies in the same region n should obviously be constant, $n\alpha$ and κ would then be zero, or tend towards zero. For the infra-red frequencies we have used, κ should be approximately constant for polar bodies.

Experimentally, our results do not confirm these curves either as to their general shape or as to the order of magnitude of the values. Indeed, as to the shape, there is a new phenomenon superimposed on that of which the theory takes account, *viz.* the appearance of absorption bands in this far infra-red, for almost all polar and non-polar liquids studied. To what do they correspond? They are produced at too low frequencies to be due to vibrational movements of atoms or groups of atomsin the molecule, such as C—H or C—CH_3. Bands corresponding to these movements are found at wave-lengths shorter than 50μ; presumably therefore the bands observed are due to folding or bending of the whole molecule, corresponding to *intra*-molecular forces or to relative movements between molecules (*inter*-molecular). This seems to be of interest in a discussion of the structure of liquids. Dilution experiments should give us the origin of these bands. For water, for example, the absorption band disappears in solution in dioxane, showing thus its intermolecular origin; [6] there is here a real structure

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[6] As to the disappearance of an absorption band with dilution and temperature measurements made in our laboratory by Dr. Mollet in the near infra-red, as yet unpublished, show that liquid alcohols exhibit at 3μ a very broad and highly absorbent band, which was attributed generally to a fundamental O-H vibration.

C_2H_5OH in CCl_4.

	Concentration *C.*	Thickness *d.*
●-●-●	0·02 mol.	5 mm.
o—o—o	0·1 mol.	1 mm.
■-■-■	0·33 mol.	0·3 mm.
▲-▲-▲	3·33 mol.	0·03 mm.

The Product $C \cdot d$ = constant.

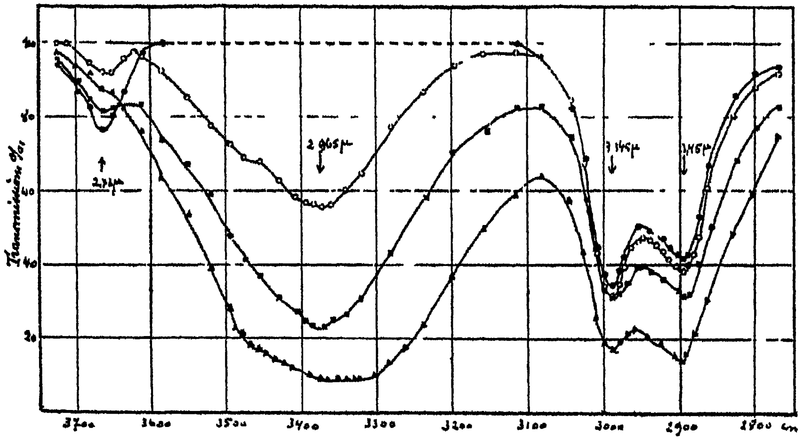

FIG. 2.

On diluting the alcohols in CCl_4 and increasing proportionally the thickness of the liquid layer, this band disappears almost completely, whilst the neighbouring C-H bands retain their intensity. On the other hand there shows up a weak band at 2·7μ previously masked by the broad band (Fig. 2). The band at 3μ

in the pure liquid, confirming both the measurements of the Raman spectra and all the arguments already adduced for considering liquids as having a structure comparable in certain respects to that of crystals.

Let us examine more closely the influence of these inter- or intramolecular bands on our results, from the point of view of the dipolar theory. The quantitative values of κ in the far infra-red are 50 to 100 times too large if we base our calculations on the values of τ obtained by hertzian measurement. Is this difference due to the superimposition of the bands masking incipient dipolar effects? At these high frequencies does viscosity lose its macroscopic sense, or are there other effects, may be many, which may come into play simultaneously?

We showed previously that in our infra-red region, even for polar bodies with small molecules, n only increases very slightly (some per cents.) when the frequency decreases, as we are too far from τ. The values of κ for six non-polar bodies we studied (vaseline and paraffin oil, hexane, carbon tetrachloride, benzene, carbon bisulphide) were of the order of some tenths to some units (in cm.$^{-1}$) whilst those of polar bodies (different alcohols, ethers, water, acetone, nitrobenzene, etc.) were from some tens to occasionally some hundreds of units.

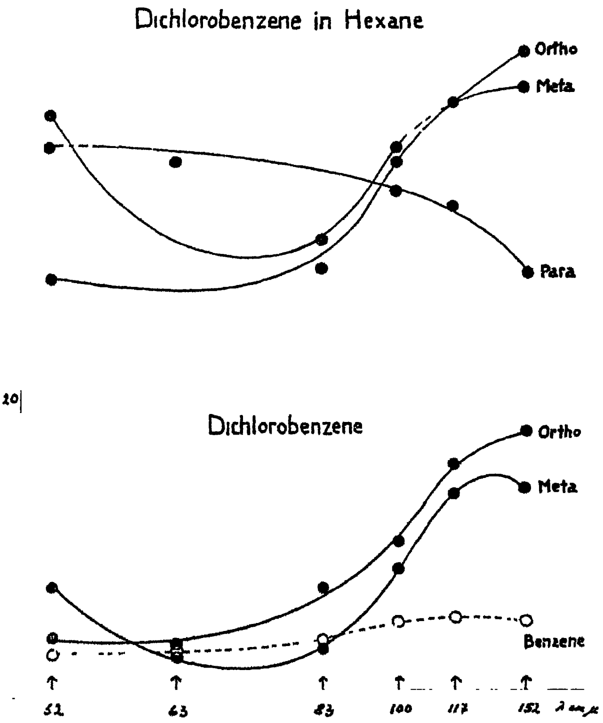

FIG. 3.

As there seemed to exist a characteristic difference between polar and non-polar bodies, we studied the three isomers of dichloro- and two isomers of dibromobenzene, in order to see whether this apparently characteristic difference was real, since these molecules are composed of the same atoms and since the null

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also disappears on raising the temperature of a relatively concentrated solution; therefore, this strong band cannot be attributed to the O—H vibration of the isolated molecule, but it shows the influence of intermolecular forces, and I believe also that the greater part of the strong absorption band of water at 3μ is of the same character. The O—H band of the isolated molecule would be the 2·7 μ band.

moment of the *para* derivatives and the high moment of the *ortho* derivatives are only due to the relative positions of the polar groupings. The dichlorobenzenes had moreover been measured in the hertzian region and the results had confirmed Debye's theory, *i.e.*, the *para* derivative with no moment absorbed no more than benzene, whilst the *ortho* derivative had a strong absorption corresponding quantitatively to the value of its moment, and the *meta* derivative an intermediate value.[7]

Nothing of the kind happens in the far infra-red; the order of magnitude of κ, apart from the absorption bands, is the same for the different isomers, whether polar or non-polar.

Table I. shows the measured transmissions and κ (as calculated, with the necessary corrections),[5] both for the pure bodies and for the solutions. For the solutions we also give κ_2 extrapolated from measurements in dilute solutions by formula (2) below. Figs. 3 and 4 show these κ values, together with those of benzene. The characteristic bands of the different isomers are clearly seen.[8]

The calculation of the extrapolated value of the extinction coefficient of the pure body (κ_2) from the values measured in solution is as follows and has a sense because it applies to absorption "bands": To a first approximation

$$\kappa_{1\cdot 2} = C_1\kappa_1 + C_2\kappa_2 \quad . \quad . \quad . \quad . \quad (2)$$

where C are volume concentrations, the subscripts 1 indicating the solvent. This formula is not quite exact from the point of view of the classical theory of absorption, but the errors only become large when the refractive indices are very different, which is not the case in the far infra-red and, in any event, are less than experimental error. When using formula (2) the laws of Lambert and of Beer are not satisfied in our measurements, since the absorption calculated from measurements in dilute solution for the pure body is stronger than that measured directly and is, moreover, not independent of the thickness of the liquid layer; these two facts accord with our earlier results. This is a new argument to the suggestion that these bands correspond to vibrations and have a fine structure which our apparatus cannot resolve; if the absorption were wholly dipolar, however, there would be no fine structure and Lambert's law would be satisfied.

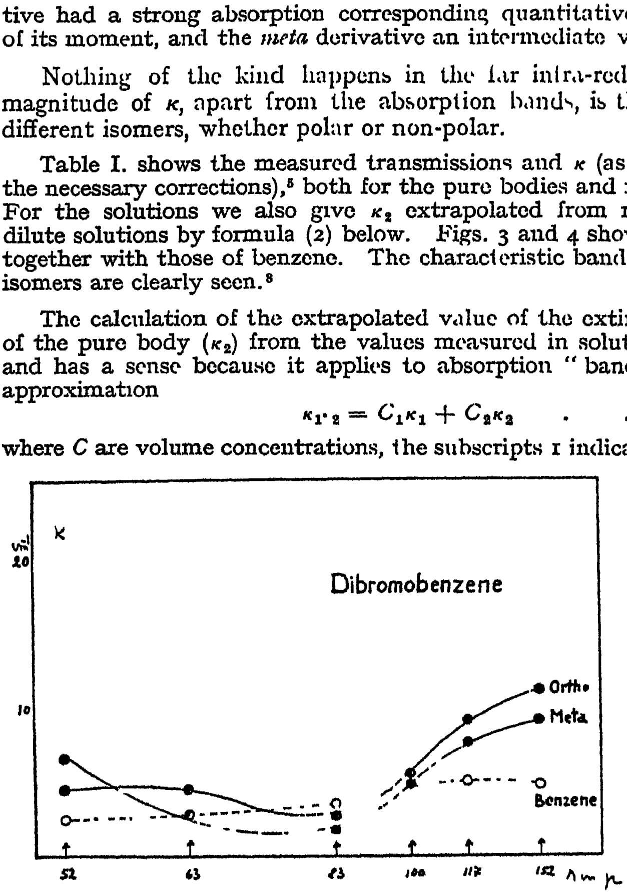

FIG. 4.

Considering now dipolar absorption, it is useful to recall more explicitly Debye's formula relating τ to the dispersion of the d.c. (or

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[7] J. Henrion, *loc. cit.*[4]

[8] The Raman effect also indicates the existence of bands for these bodies in the same region.

TABLE I.

				63.	.	100.	117.	152.
Dichlorobenzene.								
o		Tmes.	61	68	46	26	20	16
d	1·10	κpure	3·6	3·2	7·1	10	15	18
+ *o* −	13·3	Tmes.	61	—	59	—	—	—
per cent		$\kappa_{1\cdot2}$	1·2	–	1·3	2·1 *	2·6 *	2·8
d −	3·22	κ_2	2·9	-	3·7	11	15	18
m —		Tmes.	41	72	67	35	20	19
d	1·10	κpure	7·0	2·2	2·9	8·4	13	14
m —	18·9	Tmes.	14	—	62	52	45	45
per cent		$\kappa_{1\cdot2}$	3·5	—	1·9	2·8	3·4	3·4
d	2·05	κ_2	14	—	5·7	12	15	16
p —	12·3	Tmes.	54	56	—	64	67	77
per cent.		$\kappa_{1\cdot2}$	2·4	2·3	—	1·7	1·6	0·9
d −	2·05	κ_2	12	11	—	9·0	8·0	3·4
Dibromobenzene.								
o —		Tmes.	57	56	68	50	33	26
d	1·10	κpure	1·1	4·5	2·8	5·5	9·0	11·0
m		Tmes.	45	--	77	54	39	33
d	1·10	κpure	6·4	--	1·7	4·7	7·6	9·1

* Mean value for two measurements with different thicknesses.

+ Concentration in volume per cent.

++ Thickness *d* in mm.

refractive index) and to κ, treating the macroscopic viscosity conception as still always valid and making the permitted approximations for frequencies much greater than $1/\tau$, such as exist in the far infra-red, *i.e.*, $\omega\tau > 1$, where ω is the pulsation $2\pi\nu$ (the formula obviously pays no account to absorption bands)

$$\tau = \frac{(n^2_{\mathrm{IR}} + 2)(\epsilon - n^2_{\mathrm{IR}})}{\kappa c(\epsilon + 2)n_{\mathrm{IR}}} \quad . \quad . \quad . \quad . \quad (3)$$

where c is the velocity of light.

If the body is in solution the same formula can be used but ϵ, n_{IR}, and κ must be measured in solution ($\epsilon_{1\cdot2} - n_{1\cdot2}$ and $\kappa_{1\cdot2}$). When the molecules are so far separated from one another that we can neglect their interaction, *i.e.*, at sufficient dilution, (3) may be written

$$\tau = \frac{4\pi/3 \; n_0\mu^2/3kT(n^2_{\mathrm{IR}} + 2)}{n_{\mathrm{IR}} \cdot \kappa \cdot c} \quad . \quad . \quad . \quad . \quad (4)$$

where n_0 is the number of molecules dissolved per c.c. and μ the permanent electric moment of the molecule.[9]

The τ of a polar molecule is not directly comparable under different conditions of temperature and dilution, since it depends on the environment. For this reason we use formula (1) which relates τ to a^3 and brings in viscosity and temperature, so that we compare the values of the calculated molecular radii. The difference between the values of a^3 found in the hertzian region and in the infra-red, is exemplified in

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[9] This formula is analogous to that given by Debye for the hertzian region, *Trans. Faraday Soc.*, 1934, **30**, 682, formula (3).

TABLE II.

Substance.	$\kappa_{\text{min.}}$	Infra-red.		Hertzian. $\tau \cdot 10^{13}$.
		$\tau \cdot 10^{13}$.	$a \cdot 10^{9}$.	
Methyl alcohol	200	4	0·6	100
Ethyl alcohol	100	8	0·6	200
iso-amyl alcohol	30	25	0·6	1800
Glycerine	150	6	0·6	2
Nitrobenzene	20	41	0·9	205
Acetone	80	10	0·9	95

Table II., in which for κ we have chosen the lowest value in the spectral region under consideration, corresponding to the highest values of τ and a, so as to eliminate as far as possible the influence of the bands; the differences are still very large.

Another way of bringing out the dipolar origin of the absorption, which, however, also gave a negative result, is to vary the viscosity of the liquid studied. From (1) we see that on, *e.g.*, decreasing viscosity, τ should be displaced towards the large frequencies, thus obviously increasing the value of κ. This is, of course, only quantitatively true so long as the surrounding medium remains the same, *i.e.*, so long as the internal field of the liquid does not vary. This condition is reached most readily by varying the temperature; *e.g.*, an increase is accompanied by a decreased viscosity, which ought to have the above-mentioned consequences. In the hertzian region, experiment has confirmed this relationship, and a 2000-fold variation of viscosity obtained by varying temperature led to no change in a (P. Girard [4]).

Viscosity may also be modified by dissolving a viscous liquid in a much less viscous solvent; the conditions are clearly less favourable than simple temperature variation, since there is superimposed an effect due notably to diminished interaction between the molecules owing to their separation. We know from hertzian measurements that this dilution influence may be very appreciable. We have made measurements in the infra-red on very absorbent solutions of polar molecules in only slightly absorbent non-polar solvents and (although the discussion is less simple than in the case of temperature variation) deductions can be drawn from them. The variation of τ as a function of concentration is different from that observed in the hertzian region.

Table III. shows the results with a solution of *iso*amyl alcohol in CCl_4 made at one wave-length and with five different concentrations, the viscosity varying fourfold. If we compare these results with those of Girard and Abadie and especially those of Henrion and van den Grinten, the conclusions shown on Table III. can be drawn.

As for pure bodies, the value of τ in the infra-red is 40 to 100 times smaller than in the hertzian region. Further, variations of τ as a function of concentration show in our measurements a small maximum, while in the hertzian region τ increased continuously with concentration. The existence of this maximum is not surprising; if we consider κ as additive (formula (2) which is correct for absorption bands) we find that κ of the mixture is an almost linear function of concentration. Given this shape of the κ curve, if we apply to our experimental values of κ a reasoning and formulæ corresponding to the dipolar theory, it is normal that, since the polarisation curves of an alcohol, P_2, calculated from measurements at different concentrations, show a maximum, that of κ of the same solutions would also show a maximum.

TABLE III.

Conc. in vol. per Cent.	20.	40.	60.	80.	100.
***Iso*-Amyl Alcohol in Carbon Tetrachloride** (λ - 100μ).					
d in mm. . .	0·185	0·205	0·200	0·200	—
$T_{\text{mes.}}$ in per cent. .	51	58	57	51	—
$\kappa_{1\cdot2}$ . . .	11	18	24	29	40*
τ 10^{12} . . .	1·0	1·8	2·2	2·2	1·8
η . . .	0·011	0·015	0·022	0·033	0·046
κ_2 . . .	52	42	39	37	40
Nitrobenzene in Carbon Tetrachloride (λ = 100μ).					
d in mm. . .	1·65	0·485	0·203	0·203	0·210
$T_{\text{mes.}}$ in per cent. .	17·5	37	57	40	37
$\kappa_{1\cdot2}$ . . .	10	19	24	42	44
τ . 10^{12} . . .	6·1	3·9	3·3	2·0	1·9
η . . .	0,010	0·011	0·013	0·016	0·018
κ_2. . . .	45	46	40	52	44

* Mean value for two measurements with different thicknesses.

We confirmed this connection by studying a body which gives no maximum in its polarisation curve; the curve of nitrobenzene calculated from values of mixtures of this polar body in a non-polar solvent decreases regularly with dilution without showing a maximum. Our measurements in the infra-red of κ of nitrobenzene shown in Table III. confirm this and show that τ also decreases when we increase the concentration.

The polarisation curve of ethyl alcohol being a classical example with a maximum, we studied its variations of κ in the far infra-red. Table IV. shows a maximum for τ.

TABLE IV.

ETHYL ALCOHOL IN CARBON TETRACHLORIDE (λ = $100\ \mu$).

Conc. in vol. per Cent.	5.	10.	20.	40.	60.	60·7.	80.	100.
d in mm. .	1·16	0·475	0·203	—	0·115	0·115	0·115	0·115
$T_{\text{mes.}}$ in per cent.	34	44	58	–	41	40	39	29
$\kappa_{1\cdot2}$.	8·7	16	23	49*	70	73	75	102
τ . 10^{12} .	0·7	0·9	1·4	1·2	1·0	1·0	1·0	0·8
η . .	0·010	0·010	0·010	0·011	0·012	0·012	0·012	0·013
κ_2 . .	156	147	113	121	116	109	94	102

* Mean value for two measurements with different thicknesses.

For solutions of nitrobenzene, ethyl alcohol and *iso*amyl alcohol, κ obeys the additivity mixture law, except at very low concentration; this confirms the view that the absorption in these regions is due to absorption bands and not primarily to a dipolar effect.

Finally, to emphasise that viscosity does not play the part it should if the effect were of dipolar origin, we studied *sec*-octyl alcohol in a solution where its viscosity was reduced twenty-fold. Table V. shows that κ of the pure body calculated from the solution according to (2) is only at the

TABLE V.

Sec. OCTYL ALCOHOL IN HEXANE.

λ in μ.	52.	63.	83.	100.	117.	152.
d in mm. . .	0·485	0·485	0·485	0·485	0·485	0·485
$T_{\text{mes.}}$ in per cent.	41	47	51	61	68	67
$\kappa_{1\cdot 2}$ . . .	16	13	12	8·5	6·3	6·4
κ_2 . . .	75	61	55	40	29	30
κ_{pure} . .	48	47	40	36	31	26
$\eta_{\text{sol.}}$ . .	0·0045	—	—	—	—	—
η_{pure} . .	0·085	—	—	—	—	—

most 30 per cent. higher than that obtained by measurements on the pure alcohol whereas, as has been said, the viscosity is 2000 per cent.

If we treated the matter strictly from the dipolar point of view we ought to consider that the "influence of the medium" which clearly varies with dilution, would almost completely compensate the variation of viscosity, in which case the variations of κ ought also follow a linear law. But this hypothesis does not seem to us very probable and we prefer to consider that the dipolar influence is masked in the far infra-red by that due to the absorption bands.

To sum up, our results show: (1) Our curves of κ as a function of ν do not have the shape expected from the dipolar theory since there is a superimposed maximum instead of a regular curve.

(2) The absolute value of κ of polar bodies is much too high, compared with the value deduced from τ measured in the hertzian region.

(3) The variations of κ with concentration are almost linear as a function of concentration, whereas the results in the hertzian region, where the origin of absorption is dipolar would lead one to expect a different shape. We have expressed the opinion that intra- or intermolecular movements are specially responsible for the observed deviations. However, for the sake of completeness, we will enumerate other possibilities that might also play a part.

(1) As Rocard[10] has observed, at high frequencies the inertia of the molecule enters in; this, however, would decrease the theoretical κ: an effect opposite to that found.

(2) There may be, for any one molecule, several values of τ and the absorption observed in the infra-red would then correspond to a relaxation time different from that measured in the hertzian region. Let us imagine that the polar group giving the moment of the molecule is not situated in one of the axes of symmetry of the molecule, *e.g.*, as in phenol or benzyl chloride. For such molecules one might expect two relaxation periods, corresponding to rotations around the two different axes. Thus, for phenol one τ would correspond to a rotation around the large axis of the benzene nucleus and the smaller τ would correspond to rotation of the group OH around the nucleus. In the infra-red it is particularly the absorption due to the smaller τ which would make itself felt, whilst in the hertzian region the absorption due to a greater τ would be predominant. This would explain the differences between our results in the infra-red and those observed in the hertzian region and also the fact that we find the same a value (always too small) for the different alcohols, whatsoever be their chainlength.

[10] Y. Rocard, *J. Physique*, 1933, 4, 247.

(3) As a last hypothesis it is possible that, the inversion period of the electric field of the infra-red being of the order of 10^{-13} seconds, the Debye equation is no longer valid at these frequencies, inasmuch as the macroscopic viscosity law is no longer applicable. We know so little of the mechanism of viscosity in liquids, that it is possible that the viscosity law changes if the period of the movement imposed by the field on the molecules becomes of the order of that between two molecular collisions or of that of oscillations of the molecules in regard to one another.[11]

Although we believe that in the region between 50 and 150μ, the effects observed are principally due to absorption bands which mask the dipolar consequences, we can nevertheless make two observations which may have some connection with the question whether Debye's theory is valid.

Firstly, the values of κ of glycerine [5] provide the only case where the measured absorption is weaker (about 3½ times) than that calculated from measurements in the hertzian region; in this case one cannot imagine that there are superimposed bands.

The second observation relates to the refractive index of pure water and of water in solution in dioxane. Generally speaking, n scarcely varies in the spectral region in which we are working, except in the case of water where it changes from 1·67 to 2·09. This variation is sufficiently important to warrant the direct application to the pure body and to the solution of Debye's formula relating τ to n.

Rubens [12] in 1915 sought to explain his measurements in the infra-red on pure water by the Debye theory, and found the same value of τ when calculating from absorption and n. Our measurements, however, in a wider field, do not lead to the same conclusion. From κ we find $\tau = 3 \times 10^{-13}$ (Table III.), in agreement with Rubens value. From measurements of n of pure water (which attributes the whole variation of the index to a dipolar effect and not to an intermolecular vibration band effect) we calculate $\tau = 1 \times 10^{-13}$. We therefore calculated τ from measurements in dilute solution in dioxane, applying the Debye mixture formulæ directly. The index of dioxane scarcely varies (1·45 to 1·47) whilst that of a 9 per cent. solution in dioxane varies from 1·49 to 1·55; from this $\tau = 1{\cdot}7 \times 10^{-13}$. If, however, we use the higher value of κ which is more favourable for obtaining accord between the values of τ calculated by the two different ways, we find $\tau =$ about $5{\cdot}3 \times 10^{-13}$.

This lack of agreement between measurements in the hertzian region and in the infra-red and between values of τ calculated from measurements of n and κ suggests that the orientation phenomenon of molecules in an electric field of sufficiently high frequency no longer follows the law which applies in the hertzian region. The Debye formulæ were, moreover, never intended to be applied in the infra-red and it therefore seemed interesting to ascertain up to what frequencies they could be utilised without requiring supplementary corrections.

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[11] E. N. de C. Andrade, *Phil. Mag.*, 1934, **17**, 497.

[12] H. Rubens, *Verh. Deutsch. physik. Ges.*, 1915, **17**, 235.

THE DIFFUSION AND ABSORPTION OF ULTRASONICS IN LIQUIDS.

By René Lucas and Pierre Biquard.

Received in French, 7th August, 1936.

In this paper we examine the relationships which can be established between the phenomena of absorption and diffusion of elastic waves in liquids.

Although another paper will deal specially with the phenomena of absorption, their study, and especially that of diffusion, is so recent that we may perhaps first briefly recall the principal experimental results.

1. Absorption of Ultrasonics in Liquids.

Our knowledge of this subject is due particularly to the experimental work of one of us,[1] and more recently of Clayes, Errera and Sack The principal fact derived experimentally is that pure liquids have an absorption coefficient for ultrasonic waves invariably much greater (from 3 to 2000 times according to the liquid) than that to be expected from the classic theory (Stokes, Rayleigh, Kirchhoff) of the absorption of sound.

In contrast to gases there is no evidence of any change of the velocity of sound for waves of different frequencies. No systematic variation of absorption with frequency has been established; for some liquids the quantity α_a/N^2 (α_a is the coefficient of decrease of amplitude and N the frequency) increases and for others it decreases with frequency.

Table I. summarises some relevant results, which for the most part were obtained by using the diffraction of light by ultrasonics.

Substance.	$10^{17} . \frac{\alpha_a}{N^2}$ measured.			$10^{17} . \frac{\alpha_a}{N^2}$ theoretical.
	$N = 4{\cdot}77 . 10^6$.	$N = 7{\cdot}95 . 10^6$.	$N = 11{\cdot}14 . 10^6$.	
Benzene . .	867	916	806	8·66
Toluene . .	83	83	80	7·84
m.-Xylene .	63·5	75	66	8·37
Methyl acetate	156	109	82	6·78
Ethyl acetate .	85·8	77·4	62	8·26
Acetone . .	21·5	26·8	26	7·04
Chloroform .	464	490	—	10·1
Ether . .	—	55	34	8·97
Water . .	—	26	—	8·5

2. The Phenomena of Diffusion.

In seeking to explain the serious disagreement between experiment and the classic theory, one of us[2] suggested that liquid media were, elastically, not perfectly homogeneous, but constituted *acoustically*

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[1] P. Biquard ,*Thesis*, Paris, 1935.

[2] R. Lucas, *C.R.*, 1935, **201**, 1171.

disordered media. Consequently they should give rise to *diffusion* phenomena analogous to the diffusion of light.

The ready availability of ultrasonic rays made it possible to investigate this as yet unreported phenomenon. Accordingly, one of us[3] made the experiment, and established the existence of diffusion of elastic waves in pure liquids (benzene, toluene). The detection of diffused elastic waves was effected by measuring the radiation pressure exerted on a plate. For example, the pressure measured in the neighbourhood of an ultrasonic beam is of the order of 1/1000 of that measured in the primary beam (diameter of beam, 5 cm.). Reference will be made to this order of magnitude later.

3. Absorption and the Heterogeneity of Liquid Media.

A further experiment made by one of us (Lucas, *unpublished*), shows that the heterogeneity of a liquid medium plays an important part in determining the extent of absorption of elastic waves, even although only very small elements of volume may have this characteristic of heterogeneity. If equal masses of nitrobenzene and hexane are mixed, the liquid separates into two layers at about 19° C. At higher temperatures there is a single liquid phase which diffuses less and less light as the temperature is raised. The absorption of elastic waves at 25° C. is, however, much greater for this mixture (perhaps twenty fold for some cm. of thickness) than for either of the two constituents. From Drapier's measurements it is known that the viscosity of the mixture is not anomalous, and lies between that of the two constituents. On the other hand, the classic theory attributes an important rôle to viscosity in the absorption of sound in liquids.

This experiment, together with that which shows the existence of diffusion, suggests forcibly that the anomalously large absorption of ultrasonics in pure liquids may be due to their elastic heterogeneity. This point of view will be emphasised when we compare experiment with the theory of the diffusion of sound.

We must now refer to the abnormal absorption of sound, which has been studied in the case of gases and has been satisfactorily explained by Einstein, H. O. Kneser, D. G. Bourgin, E. Grossmann, etc. There is, however, an essential difference between gases and liquids, in that there is no dispersion of the velocity of sound in liquids, although this is notably so in gases. On the other hand, the theory developed in the case of gases does not relate the absorption and the heterogeneity of the elements of volume of the gaseous medium. For various reasons, we are concerned, in the case of liquids to consider carefully this heterogeneity of the different elements of volume.

The most general study, but a very complex one, involves taking into account simultaneously the breaks or fluctuations in the density and in the elastic parameters of the elements of volume of a liquid, and thus establishing the manner in which an elastic wave is damped in such a medium.

In order to minimise the difficulties we consider separately two cases:

(1) The fluid has fluctuation of density, and the velocity of the elastic waves remaining the same at various points, we neglect diffusion.

(2) The fluid is considered as a medium having fluctuations in the compressibility of its various elements of volume.

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[3] P. Biquard, *C.R.*, 1936, **202**, 117.

4. * Absorption of Sound in Liquids having Fluctuations of Density (at Constant Velocity of Sound) in the Absence of Diffusion.

Given a ray of plane elastic waves propagated in the direction *ox*, and given that $a_0 = A \sin \omega(t - x/V)$, its amplitude in a homogeneous medium gives no absorption ; given further that, at certain places, the local density ρ differs from the mean value ρ_0 ; at those places the amplitude will differ from a_0 and will be, to a first approximation, $a = ma_0$, where $m = \sqrt{\rho_0/\rho}$. As simplification we suppose that density variations are independent of time, so that the parameter m depends only on the co-ordinates of space. The velocities of the different parts of the fluid, during the passage of the sound, will then have a single component along *ox*. Consider now the effect of viscosity. In order to calculate the damping of the waves we utilise the energy dissipated per unit volume by the effect of the forces of viscosity. The expression for this power dissipated in heat, is according to Stokes and Rayleigh[4]

$$W = \lambda\theta^2 + \eta\Big[2\Big(\frac{\partial u}{\partial x}\Big)^2 + 2\Big(\frac{\partial v}{\partial y}\Big)^2 + 2\Big(\frac{\partial w}{\partial z}\Big)^2 + \Big(\frac{\partial w}{\partial y} + \frac{\partial v}{\partial z}\Big) + \Big(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}\Big)^2 + \Big(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y}\Big)^2\Big],$$

where $\theta = \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}$, λ and η being Stokes' coefficients (η the usual viscosity coefficient and u, v, w components of the fluid velocity along the co-ordinates x, y, z.

We have, then, $u \neq 0$, $v = 0$, $w = 0$, and, consequently,

$$W = (\lambda + 2\eta)\Big(\frac{\partial u}{\partial x}\Big)^2 + \eta\Big[\Big(\frac{\partial u}{\partial z}\Big)^2 + \Big(\frac{\partial u}{\partial y}\Big)^2\Big]$$

$$u = \frac{\partial a}{\partial t} = m\frac{\partial a_0}{\partial t}.$$

Assuming, as a further simplification, that the variations of m for the different directions are isotropic

$$\Big(\frac{\partial m}{\partial x}\Big)^2 = \Big(\frac{\partial m}{\partial y}\Big)^2 = \Big(\frac{\partial m}{\partial z}\Big)^2 = \frac{1}{3}\Big(\frac{\partial m}{\partial r}\Big)^2, \quad r^2 = x^2 + y^2 + z^2.$$

In an element of volume $d\tau = dx\,dy\,dz$ the power lost will be

$$dW = \Big\{(\lambda + 2\eta)\frac{m^2}{2}\Big(\frac{Aw^2}{V}\Big)^2 + A^2w^2\Big(\frac{\lambda + 4\eta}{3}\Big)\Big(\frac{\partial m}{\partial r}\Big)^2\Big\}$$

which is, per unit of volume,

$$W = \frac{1}{\tau}\int_0^\tau dW = \frac{\lambda + 2\eta}{2}\Big(\frac{Aw^2}{V}\Big)^2\frac{1}{\tau}\int_0^\tau m^2 d\tau + A^2w^2\frac{\lambda + 4\eta}{3}\frac{1}{\tau}\int_0^\tau\Big(\frac{\partial m}{\partial r}\Big)^2 d\tau.$$

The quantity $\frac{1}{\tau}\int_0^\tau m^2 d\tau$ may be related to the local condensation s of the fluid, defined by $\rho = \rho_0(1 + s)$

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* Parts 4 and 5 are taken from the work of one of us. R. Lucas, *C.R.* 1936, *J. Physique* (in the press).

[4] Rayleigh, *Phil. Trans.*, 1866, **156**, 249.

$$m^2 = \frac{1}{1+s} \text{ and } \frac{1}{\tau}\int_0^\tau m^2 d\tau = \frac{1}{\tau}\int_0^\tau (1 - s + s^2 - s^3 \quad . \; .)d\tau.$$

Eliminating all but the second order, and remembering that $\frac{1}{\tau}\int_0^\tau s d\tau = 0$,

$$\frac{1}{\tau}\int m^2 d\tau = 1 + \frac{1}{\tau}\int_0^\tau s^2 d\tau.$$

For convenience, we can consider that the density fluctuations are the same as those brought about by a system of longitudinal waves (Debye) and relate $\frac{1}{\tau}\int_0^\tau s^2 d\tau$ to the density of energy of the liquid waves, equivalent to the thermal energy.

If E is this density, and β the coefficient of isothermal compressibility $\left(\beta = -\frac{1}{v}\frac{\partial v}{\partial p}\right)$, we have, adopting the expression proposed by Debye,[5]

$$E = \frac{1}{\beta}\frac{1}{\tau}\int_0^\tau s^2 d\tau = \frac{4\pi}{V^3}\int_0^{\nu_l}\frac{h\nu^3}{e^{\frac{h\nu}{KT}} - 1}d\nu.$$

ν_l is the frequency limit of the waves which can exist in the liquid.

Finally, we obtain the damping coefficient α_a of the amplitude

$$Ae^{-\alpha_a x}\cos\omega\left(t - \frac{x}{V}\right)$$

$$\alpha_a = \frac{W}{\rho_0 V . A^2\omega^2} = \left(\frac{\lambda + 2\eta}{2}\right)\frac{\omega^2}{\rho_0 V^3}\left[1 + \frac{4\eta\beta}{V^3}\int_0^{\nu_l}\frac{h\nu^3 d\nu}{e^{\frac{h\nu}{KT}} - 1}\right] + \frac{\lambda + 4\eta}{3\rho_0 V}\frac{1}{\tau}\int_0^\tau\left(\frac{\partial m}{\partial r}\right)^2 d\tau$$

instead of $\alpha_a = \frac{\lambda + 2\eta}{2}\frac{\omega^2}{\rho_0 V^3}$ of Stokes' theory. We can relate λ and η by Stokes' equation $3\lambda + 2\eta = 0$, which suggests that an isotropic compression or dilatation exerts no work.

The first correction $\frac{4\pi\beta}{V^3}\int_0^{\nu_l}\frac{h\nu^3 d\nu}{e^{\frac{h\nu}{KT}} - 1}$ becomes infinite near the critical point, if we adopt the value ν_l of Debye,

$$\nu_l = V\left(\frac{9N\rho_0}{4\pi M}\right)^{1/3}$$

where N is Avogadro's number and M the molecular mass. Generally speaking, its magnitude is insignificant in regard to unity for normal liquids at ordinary temperature when this value of ν_l is adopted; it depends largely on the frequency limit since, for very large ν_l the correction reaches several tens. The question of the limitation of ν_l to the preceding value will doubtless need to be examined anew.

Evaluation of the second correction

$$\frac{\lambda + 4\eta}{3\rho V}\frac{1}{\tau}\int_0\left(\frac{\partial m}{\partial r}\right)^2 d\tau$$

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[5] P. Debye, *Ann. Physik*, 1912, **29**, 789; see also L. Brillouin, *Ann. Physique*, 1922, **17**, 88.

is delicate, and it may be treated as a function of structure. The preceding evaluation leads then to a value of α_a such that

$$\frac{\alpha_a}{N^2} = A + \frac{B}{N^2}$$

where A and B are constants and N is the frequency.

5. Fluid having Elements of Volume with Different Compressibilities. Diffusion of Sound.

This problem is not absolutely distinct from the preceding one ; the constancy of the velocity of sound $V = \frac{1}{\sqrt{\rho\mu}}$ where μ is the adiabatic compressibility; embodies, in effect, fluctuations of μ corresponding to fluctuations in ρ.

The most simple case to study is that of a homogeneous fluid medium within which there are volumes (*e.g.* spherical) limiting portions of fluid having a compressibility μ differing from μ_0 of the outside medium. If ϵ is the radius of one of these spheres, ϵ will undergo periodic variations during the passage of the wave. When ϵ is small relatively to the wave-length, one can readily evaluate the mechanical power dissipated by diffusion by one of these spheres (*cf.* the pulsating spheres of Bjerkness). If the " pulsation " is due to passage of a wave of amplitude

$a_0 = A \sin \omega(t - x/V)$ we find, for the power diffused :

$$W_d = \frac{2}{9}\,\frac{\epsilon^6 A^2 \omega^6}{V^5 \mu_0}\left(\frac{\mu - \mu_0}{\mu_0}\right)^2.$$

From this, the coefficient of weakening of the exciting wave is calculated. If there are n analogous elements per unit of volume

$$\alpha_{a(\text{diffusion})} = \frac{W_d}{\rho_0 V A^2 \omega^2} = \frac{2}{9}\,\frac{\epsilon^6}{V^4}\omega^4 n\left(\frac{\mu - \mu_0}{\mu_0}\right.$$

It can be shown from this that the damping of audible waves on passing through layers of air enclosing drops of water (rain, cloud) is insignificant, as is shown by actual observation. On the other hand, the absorption exercised on a beam of ultrasonics by the traverse of water containing microscopic bubbles of air is quite considerable, as is also known.

If now we attribute fluctuations of compressibility of the liquid medium to thermal agitation alone, theory shows how to obtain α_a from thermodynamic parameters.

In effect, $\rho\mu = \rho_0\mu_0$, whence $\frac{\rho - \rho_0}{\rho_0} = \frac{\mu_0 - \mu}{\mu_0}$.

Now, from the theory of fluctuations

$$\overline{\left(\frac{\rho - \rho_0}{\rho_0}\right)^2} = \frac{RT\beta}{N\Delta v}$$

R being the gas constant, N Avogadro's number, T absolute temperature, β iso-thermal compressibility, and Δv an element of volume.

Here, $\Delta v = \frac{4\pi}{3}\epsilon^3$ and $n = \frac{1}{\Delta v}$,

so that $\alpha_a = \frac{2\pi^3}{\Lambda^4}\,\frac{RT\beta}{N}$, where Λ is the wave-length. It is interesting to derive this relationship from that which relate to the absorption of light by diffusion, in cases where there is no optical molecular anisotropy :

$$(\alpha_a)_{\text{lumière}} = \frac{4\pi^3}{3\lambda^4}\frac{RT\beta}{N}(n^2 - 1)^2,$$

n being the refractive index and λ the wave-length of light in vacuo.

The comparison shows that the relationship giving α_a for sound predicts a *diffusion effect for elastic waves in liquids of an order of relative magnitude comparable to the diffusion of a beam of light of the same wave-length* (in vacuo).

For such a liquid as toluene, the order of magnitude observed by P. Biquard for the diffusion of ultrasonic is incomparably greater than that which would be expected. To explain this, we assume that in the body of the liquid there are certain elements of volume (*e.g.* crystalline molecular aggregates) having very different compressibilities from those of the normal liquid (*e.g.* ten times smaller). This conclusion is in agreement with other points of view explaining various phenomena (diffraction of X-rays, etc.).

On the other hand, if absorption by diffusion were the sole cause of the weakening of the waves, the coefficient α_a ought to increase with the fourth power of the frequency, as with light, but this is not so.

We must therefore consider the absorption of elastic waves as due to viscosity, bearing in mind the possibility of the existence in the body of the liquid of elements of different compressibility. Analytically, the problem is very complex, for the distribution of fluid velocities around an element of volume analogous to a pulsating sphere, bearing in mind the exciting waves, is very complicated, and no definite conclusions can be formulated.

When making an evaluation similar to that suggested in paragraph 4 we find that the absorption coefficient due to viscosity forces depends on three terms α_1, α_2, and α_3.

α_1 corresponds to the classic term of Stokes, or to that term modified as in paragraph 4. α_2 represents the dissipation as heat of the diffused radiation, and is small relatively to the frequency effect. Finally, α_3 indicates the effect of interaction between the components of velocity of the primary exciting waves, and those of velocity in the neighbourhood of spherical pulsating elements ; it is the sum of the two others, one $\epsilon^3\omega^2$ and the other $\epsilon^3\omega^3$. Hence, if the diffusing elements of volume are sufficiently small, the part played by α_3 may become large relatively to the diffusion term $\epsilon^6\omega^4$. In this case, the diffusion effect will signify a damping mechanism much more important than that effect in the same fluid if the latter is treated as having no viscosity.

6. Conclusion.

The diffusion of elastic waves by liquids can only be explained by the presence of elements of volume having a compressibility very different from the mean compressibility in the liquid under consideration.

Attempts to explain the large anomalous absorption of ultrasonics meet with serious difficulty from the point of view of the Stokes' theory but appear to have a greater chance of success on this hypothesis.

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ABSORPTION OF ULTRASONIC WAVES IN LIQUIDS.

By J. Claeys, J. Errera and H. Sack (*Brussels*).

Received 3rd September, 1936.

The study of the velocity and absorption of sound may be of some interest in respect to the structure of liquids. It admits the possibility of drawing conclusions on the compressibility, the viscosity and other characteristic constants of the liquid. But while ordinary measurements yield, in general, " static " values of these constants, the investigation of the propagation of sound procures us values that correspond often to very quick changes of state. So, *e.g.*, in a wave of the frequency 10^7 one adiabatic compression lasts 10^{-7} sec. One cannot predict whether the values determined in processes of such high frequency will coincide with the static values. It seemed therefore worth while to experiment on this subject.

Before discussing the results obtained we shall briefly describe the experimental arrangement. The results being rather unexpected it seems to us important to give here some experimental details.[1]

Apparatus.

The object of the present work was the measurement of the absorption of sound in liquids at various frequencies. The extinction coefficient κ is defined by:

$$I = I_0 e^{-\kappa d} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where I is the intensity of the plane accoustic wave in a distance d from the point where the intensity is I_0. Quantitative determinations of κ have been carried out by Biquard [2] and by Sörensen.[3] Unfortunately the results of the latter seem rather doubtful, as we shall see later on, and therefore we shall compare our results only with those of Biquard, who measured κ at frequencies of $\nu = 4{\cdot}7$ to $11{\cdot}1 \cdot 10^6$. He used an optical method based on the diffraction of light by ultrasonic waves in liquids, and for H_2O he also used a "radiation-pressure" method (Lord Rayleigh). In this range he found κ/ν^2 to be independent of frequency, except for methyl- and ethylacetate.

Our measurements were made at frequencies $\nu = 0{\cdot}3$ to 5×10^6, *i.e.*, over a range of 4 octaves, and therefore complete the work of Biquard. We used a pressure method. The scheme of the apparatus is given in Fig. 1. The quarts Q emitting the ultrasonic waves is placed on a piece of lead L in a vessel containing good insulating oil. It is connected to a powerful radio wave emitter. A long tube T, closed at the bottom with a thin glass-plate P is dipped into this vessel. This tube contains the liquid under investigation. The plane wave emitted by the quartz in the oil travels perpendicularly upwards through the glass plate into the liquid. The reflector R (of Al) avoids regular reflection on the surface of the liquid. In the liquid is suspended a metallic sphere S, attached by a thin thread to a torsion-balance B, by which the radiation-pressure (proportional to

[1] More details will be given later in a publication elsewhere.

[2] P. Biquard, *Thèse*, Paris, 1935.

[3] C. Sörensen, *Ann. Physik*, 1936, **26**, 121.

the intensity of the wave) exercised on the sphere is measured. The balance may be changed in height by a movable stand St, and so the pressure may be determined at different distances from the bottom of the tube.

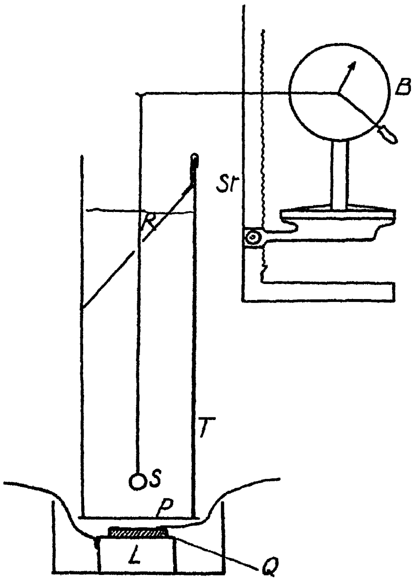
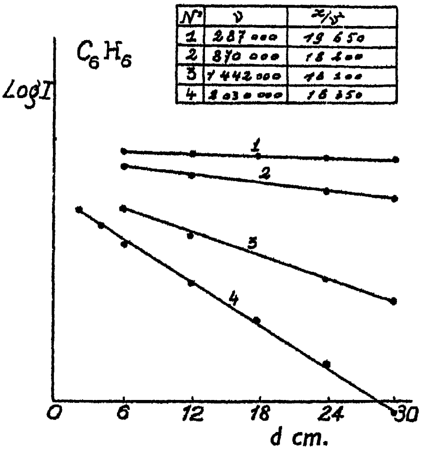


FIG. 1.

We used a sphere instead of the traditional plane disk in order to avoid the possibility of standing waves between the bottom of the tube and the body which serves for the pressure measurements. At the same time this system permits control to ensure that the sphere is always in the centre of the sound-beam. If it is decentred there arises a lateral force and the thread deviates from the vertical position.

The separation of the quartz from the liquid by the glass plate diminishes the possibility of errors from convection-currents in the liquid.

Great importance must be attached to the dimensions of the tube; if it is too narrow the values measured may be falsified by the influence of the walls of the tube or by resonance phenomena. In general we used a tube of 12 cm. diameter. In order to ascertain whether or not there is an influence of the walls we often put into this tube a second one of 10 cm. diameter. We also changed the material of the walls (glass or copper). Finally we worked with several plates P of different thicknesses and we changed the distance of P from the quartz.



N°	ν	κ/ν^2
1	287 000	19 650
2	870 000	18 400
3	1 442 000	16 100
4	2 030 000	16 350

FIG. 2.*

The choice of too small a tube is very probably the cause of the discrepancy between the values of Sörensen and those of Biquard and ours. In fact he used a tube of 8 cm. diameter. In the case of C_6H_6 he measures $\kappa = 0{\cdot}017$ for $\nu = 2{\cdot}87 \times 10^5$; we found, at the same frequency $\kappa = 0{\cdot}0017$ (in agreement with Biquard, see Table I.) in our 12 or 10 cm. tube, but 0·076 in a 6 cm .tube. For H_2O: Sörensen found 0·017 (8 cm.); we found 0·030 (6 cm.) and $< 0{\cdot}0004$ (12 cm.). At high frequencies the discrepancies get smaller, as one may expect.

The diameter of the sphere was 2·0 cm.; in some experiments we employed a cone with a base of 2·5 cm. We also changed the initial intensity of the wave. The radiation-pressure at 4 cm. from the bottom varied between 1·3 and 7·5 dyn./cm.^{2} We never found differences in the results.

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* κ/ν^2 in 10^{-17}.

An important control consists in measuring the pressure at different distances d and in verifying if the measured values obey the exponential law.[4] Fig. 2 gives an example (C_6H_6 at 4 frequencies): log I is plotted against d; the experimental points lie closely on straight lines, as they should. Very near the bottom ($d < 4$ cm.) we found deviations from the straight line, even with small intensities. For the calculation of κ we only considered the linear part.

The temperature was in general that of the room, *i.e.*, $t = 16$ to 20° C. During the emission of the waves the temperature of the liquid rose less than 1·5°. Preliminary measurements of the dependence of κ on t showed that, in general, this is unimportant and that the errors due to other causes predominate. We estimate the accuracy of κ to $\sim$ 5–10 per cent., except for very small values of κ (*e.g.*, H_2O), where it may decrease to 20 per cent.

TABLE I.—VALUES OF $\kappa/\nu^2 \times 10^{17}$

$\nu \times 10^{-6}$. Substances.	0·287.	0·870.	1·442.	2·030.	Biquard. 4·77 to 11·14.	Theoretical
H_2O	—	—	$\sim$65	$\sim$80	53·2	17
CCl_4	—	—	$\sim$30	$\sim$14*		32
C_6H_6	1900	1950	1800	1900	1720	17
CS_2	19·200	22·000	-	-	-	10
CH_3COOCH_3	—	1100	1100	1200	312·6 to 104·4	14

* $\nu = 3·16 \times 10^6$.

Results.

It is not possible to compare κ for different frequencies, κ varying in general with the frequency. In the classical theory of sound κ should be proportional to ν^2, at least so long[5] as ν is not too high ($\nu < 10^{10}$); κ/ν^2 should be a constant. We shall first examine our results from this point of view. In Table I.[6] are given some of our values for pure liquids, as well as the corresponding values of Biquard and those calculated by the classical theory. We see that the ν^2 law is followed in our region and that our κ/ν^2 coincide quite well with Biquard's values. (Methyl acetate forms an exception, in that our κ/ν^2 is much greater; we shall revert to this later.) But the most striking result is that the experimental values are in general much greater, for CS_2 even 2000 times, than the calculated ones.

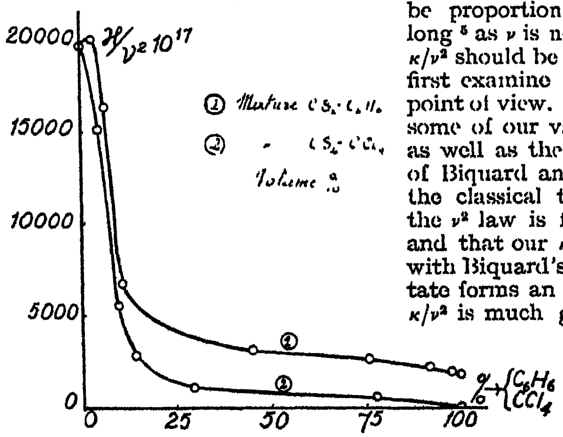

FIG. 3.

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[4] Sörensen measured at one distance only; we found that in narrow tubes the exponential law is very often not followed.

[5] See Y. Rocard, *Propagation du son*, Paris, 1935.

[6] J. Claeys, J. Errera and H. Sack, *C.R.*, 1936, **202**, 1493.

In the second place, we studied the influence of dilution, especially in the cases of very great κ. Fig. 3 shows κ/ν^2 as a function of the concentration for $CS_2 + CCl_4$ and $CS_2 + C_6H_6$. The mixture of $C_6H_6 + CCl_4$ gives a similar curve. The characteristic of these curves seems the sharp drop at the high concentrations of CS_2. We also studied some aqueous salt solutions. Table II. reproduces our results. ($\nu = 3{\cdot}7 \times 10^6$.) The addition of salt makes κ increase; but there is no marked influence of the valency of the dissolved ions.

TABLE II.—$\kappa/\nu^2 \times 10^{17}$ OF SALT SOLUTIONS.

Concentration in gm. equiv./litre.	NaCl.	Na_2SO_4.	$MgCl_2$.	$MgSO_4$.
⅛	70	—	—	—
¼	95	80	95	85
½	120	100	135	115
1	165	140	205	175
2	190	—	260	220
4	—	—	360	300

Finally, we searched for an example where the ν^2-law is not followed. The case of methyl acetate seemed to be of interest in this respect. Between $\nu = 2{\cdot}5$ and $0{\cdot}3 \times 10^6$, κ/ν^2 is constant, but its value is higher than that of Biquard. In order to clear up this point we made a series of measurements in the frequency range between $2{\cdot}5$ and 5×10^6. The results are shown in Fig. 4, together with those of ethyl acetate. We have plotted κ against $\log \nu$ including the points of Biquard (+). The dotted lines represent κ/ν^2. Nearly all measurements were made in the 12 and 10 cm. tube. It is very surprising to find a maximum for κ which corresponds to a sharp drop in κ/ν^2.

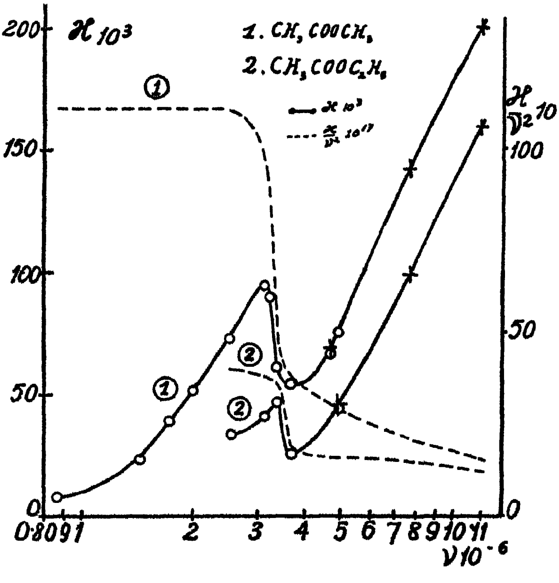

FIG. 4.

Discussion.

In seeking to explain our results we have to take into account two phenomena: (1) the discrepancy between κ/ν^2 exp. and calc.; and (2) the anomalous variations of κ with frequency. In the classical theory which served as a basis for the calculated values, the absorption is mainly due to viscosity. The formulæ are deduced on the assumption that the amplitude (intensity) of the wave is infinitely small and that we have to deal with an ideal continuum. In the experiments the amplitude may assume considerable magnitude and Biquard considered in detail the influence of this fact. But the agreement with the exponential law and the independence of κ on the initial intensity seem rather to indicate that the lack of agreement is not to be looked for in this direction. Lucas [7] and Biquard [8] sought to explain the high κ-values by a diffusion of the ultrasonic wave, but their results seem not yet conclusive.

For all these reasons we are more inclined to attribute the discrepancies to the non-ideal structure of the medium. Our first idea was to connect them with the quasi-crystalline structure of the liquid. But this point of view does not seem to be fruitful. We know, for example, that the "inner field," which may be considered as a certain measure for the deviation from the ideal state, is very great in water and less in benzene. On the contrary, in our case the rate of the measured κ/ν^2 to the calculated one is much greater for C_6H_6 (factor 100) than for H_2O (factor 3). We may also consider the fine structure of the Rayleigh-radiation which is also intimately connected with the crystalline structure of liquids. Ramm [9] observed this fine structure with good intensity for both CCl_4 and CS_2, while we find practically no discrepancy for CCl_4 and a tremendous one for CS_2. There is no analogy, then, between our results and those of other researchers on the quasi-crystalline structure of the liquid.

By such considerations we were led finally to the conception that the discrepancies may be due to a change of the adiabatic compressibility with frequency. We know that in the case of gases this point of view had been very fruitful (theory of Kneser).[10] There one also finds too high an absorption, which shows an "anomalous" frequency-dependence. The explanation is given by the fact that at sufficiently high frequencies the specific heat (and in consequence the adiabatic compressibility) changes: the excitation of atomic vibrations needs a certain time and at high frequencies the part of the specific heat corresponding to these excitations disappears. In the case of liquids we should think that similar phenomena may be possible. As the interaction between the molecules in the liquid state is more intensive the "time of relaxation" will be shorter than in the gaseous state.

As in the case of gases, one cannot predict whether the effect will be great or not; the characteristic constants varying from substance to substance, we may expect also in the case of the liquids to find different absorptions for different substances.

In the case of liquids the problem is more complicated: not only do the intra-molecular vibrations contribute to the specific heat but probably also intermolecular ones. Moreover it is also possible that even the isothermic compressibility is a function of the frequency. In order to throw light on this point we started measuring the absorption of Hg where no intramolecular vibrations are possible. Unfortunately we have not yet arrived at conclusive results. Of course one would expect to find also a dispersion of the velocity at the same time as an "anomalous" absorption. In the literature there are no indications in this sense; we intend to measure the dependence of the velocity on frequency of some compounds, especially of the acetates.

For the sake of completeness we should like to state that other possibilities for the explanation of the discrepancies are not excluded. Thus, it may be possible that transverse waves exist even in liquids, and especially when their quasi-crystalline structure is very pronounced,[11] and that in this way energy may be dissipated. That the viscosity itself (which enters into the classical formula) changes at the frequencies in question, is only slightly probable, as there are no anomalies observed, *e.g.*, in the case of the anomalous electric dispersion.[12]

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[7] R. Lucas, *C.R.*, 1935, **201**, 1172.

[8] P. Biquard, Ibid., 1936, **202**, 117.

[9] W. Ramm, *Physik. Z.*, 1934, **35**, 111, 756.

[10] For literature see Grossmann: *Hdb. Exp. Physik*, 1934, 17, 401; Y. Rocard, *loc. cit.*[5].

In conclusion, we may say that sound absorption measurements lead to discrepancies between the values calculated by the classical theory and the observed ones, in regard to the magnitude as well as to the frequency-dependence. A good hypothesis for further work seem to be that of a frequency dependence of the adiabatic compressibility.

We are greatly indebted to the " Fonds National de la Recherche Scientifique " (Belgium) for the apparatus.

*GENERAL DISCUSSION.**

Dr. H. Sack (*Brussels*) said : (1) If we make the time-lag of the specific heat responsible for the observed absorption as in the case of gases, then we can easily estimate the effect. Two unknown factors enter into the calculation, *viz.*, the relaxation time and that part of the specific heat which shows the relaxation phenomenon. If we assume that the dispersion of velocity due to the velocity of sound is no greater than 1 per cent. (an assumption that seems in accord with experiments), the relaxation time may be estimated from the observed extinction-coefficient ; it is 10^{-7} to 10^{-10} sec. This theory accords with the fact that for frequencies smaller than that, ν_0, corresponding to the relaxation time the χ is proportional to ν^2 (the influence on the velocity gets only detectable in the immediate neighbourhood of ν_0). But we should like to emphasise that in the case of liquids, in contrast with the case of gases, the compressibility itself may, and will, probably, show a time effect.

(2) Continuing our measurements on mixtures, we investigated solutions and mixtures of methyl acetate with ($C_6H_6 + CCl_4$) in all of which the drop in χ/ν^2 appears (even for the opalescent mixtures) at nearly the same frequency as for the pure substance. The χ of the opalescent mixture is somewhat higher ($\sim$ 3 times) than that of the transparent ones.

(3) If the structure of liquids is considered as quasi-crystalline, the fine structure of the Rayleigh radiation must be ascribed to crystalline formations (" blocs ") in the liquids. Since the velocities of ultrasonic waves calculated from this fine structure are the same as those of normal acoustic waves, we may conclude that the compressibility in these " blocs " must be the same as the average compressibility of the whole liquid.

Professor J. Errera (*Brussels*) said : By saying that the large O—H band at about 3 μ in alcohols are due to intermolecular forces, I meant that they are due not only to forces between the H and the O of the same molecule but also to linkages of H belonging to one molecule and O belonging to another ; *i.e.*, an intermolecular hydrogen bond similar to the intramolecular bond of chelated compounds.[13]

Dr. E. Bartholomé (*Göttingen*) said : In addition to the spectroscopic evidence the fact [14] that the 3μ band of alcohol is the valency vibration of the O—H bond in the separate alcohol molecule, follows from the observation that this band (1) is also present in gaseous CH_3OH at pressures of

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[11] L. Brillouin, *J. Physique*, 1936, **7**, 153.

[12] See J. Errera, *this vol.*, p. 120.

* On the four preceding papers.

[13] *Cf.* N. V. Sidgwick, *The Electronic Theory of Valency*, and J. Errera and P. Mollet, *J. Physique*, 1935, **6**, 261.

[14] E. Bartholomé and H. Sachsse, *Z. physik. Chem.*, *B*, 1935, **30**, 40.

50 mm., and (2) will be changed on substitution of the alcoholic hydrogen by deuterium to $4 \cdot 2\mu$, *i.e.*, in the proportion $\sqrt{2}$ to 1.

Mr. C. R. Bailey (*London*) said: Professor Errera describes Dr. Mollet's work on the 3μ band of ethyl alcohol in carbon tetrachloride solution, and attributes it to intermolecular forces. A band of such intensity is almost certainly due to a fundamental mode with a high force constant, and an application of the Badger rule relating force constants and interatomic distances indicates that the actual distance involved is too small for any type of intermolecular linking. The only possible type of bond with masses sufficiently small to give a vibration in this region is the hydrogen bond, but the force constant in this case must be very small, since there is no evidence of such a high frequency in the obvious case of hydrogen fluoride, which is associated in the vapour state at room temperature. The heat of dissociation of a hydrogen bond is some 6 kcals. per mol.; the N—N link in the true molecule N_2O_4 has the corresponding heat of 13 kcals.; the vibration concerned is 283 cm.$^{-1}$, and the force constant [15] is $1 \cdot 5 \times 10^5$ dynes/cm., and it is not unlikely that any vibration due to a hydrogen bond would appear in the same region.

It is unfortunate that other observers obtain results directly contrary to those of Dr. Mollet. Malone [16] finds that molecular association can, indeed, be traced by observations on this ethyl alcohol band at 3μ, but that in benzene-alcohol mixtures the intensity of the band is always greater than in the pure alcohol. Kinsey and Ellis [17] also find that the harmonic of the corresponding band in methyl alcohol is sharper in CCl_4 solution than in the pure alcohol. Hence we find that intermolecular association so far from being the origin of the band actually reduces its intensity.

I believe that much information with regard to the liquid state will eventually be obtained from a careful observation of the change in characteristic spectroscopic frequencies which sometimes accompanies a change in state. The occasionally unexpected nature of the observations may be illustrated by reference to carbon disulphide and benzene. Dr. Angus and I have shown that whereas the symmetrical valence frequency ν_1 undergoes no change in the passage from gas to liquid, the asymmetrical valence frequency ν_3 has the value 1521 cm.^{1} in the gas, and 1479 cm.$^{-1}$ in the liquid, a decrease of 42 cm.$^{-1}$. The intensity of change of electric moment in this vibration is markedly affected by the presence of neighbouring molecules.

The symmetrical D_{6h} model for benzene has a centre of symmetry, and consequently bands active in the infra-red are forbidden in the Raman effect, and *vice versa*. This is found to be true for the gas, but the intense electric fields produced by the orientation of the disc-shaped molecules at distances of some 3Å. lead to a suspension of the selection rules, and "forbidden" bands coincident with Raman lines appear in the infra-red spectrum of the liquid.

Mr. J. D. Bernal (*Cambridge*) said: I am inclined to agree with M. Magat about the temperature changes in water at 50°. Free rotation may take place, but I do not consider the change over to free rotation to be in any sense a transformation of the liquid, that is something taking place at a definite temperature, but rather that the number of free rotating molecules in the liquid increases continuously as the temperature is raised and becomes a mere proportion of the number of molecules at the temperature of about 50° C. The strength of the 3600 band in the Raman structure might be used as some measure of the number of freely rotating molecules.

A possible explanation of the anomalies observed in the absorption of ultrasonic waves in liquids is that at these frequencies the normal condition of the liquid not only in respect of specific heat but also to compressibility is itself a function of the frequency. The equilibrium state in a liquid is only maintained by a continual set of changes of configuration but this configurational change occurs in a period of time long compared with that of intermolecular vibrations. It is conceivable, though difficult to prove, that for a very short pulse of the orders of frequency studied by the authors, *i.e.*, about a millionth of a second the configuration of the liquid has no time to change itself appropriately. The result would be that considerable disturbance would occur in the passage of the wave. It is true that in these cases one would expect dispersion to accompany absorption and this has not been observed. But until we have an adequate theory of the effect it would be unsafe to reject such a possibility out of hand.

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[15] Sutherland, *Proc. Roy. Soc., A*, 1933, **141**, 361.

[16] *Nuov. Cim.*, 1935, **12**, 441.

[17] *Physic. Rev.*, 1936, **49**, 105.

It is clear that M. Errera was using the word " inter-molecular " for the origin of the band at 2·965 μ in a different sense than that of his critics. As I see it he wished to imply only that it was due to the influence of one molecule on another and not to the gross vibration of one molecule against another. What he has shown in this case seems to be of the greatest value. The band at 2·73 μ is due to the free (OH) vibration. At higher concentrations some of the (OH) groups become joined by what I have called hydroxyl bonds to (OH) groups in neighbouring molecules. The proton is now bound less strongly to its original oxygen and the wavelength changes to 2·965 μ. This frequency however is no longer a single frequency but a wide band due to the variety of different configurations which the two alcohol molecules can have in respect to one another. What is specially significant however is that there is no gradual transition between the free hydroxyl frequency and the hydroxyl bond frequency. Instead of that, the intensity of one decreases and the other increases without any absorption appearing at intermediate wave-lengths. This can only mean that the hydroxyl bond is a definite entity and that at any given concentration some alcohol molecules are free, and others are attached by hydroxyl bonds, but that no intermediate state is possible.

Dr. M. Magat (*Paris*) said, with reference to Professor Henri's paper: It appears to me very difficult to assume, that ordinary van der Waals forces (which in this case are only London forces) can explain the very strong bands Professor Henri observed. These forces are smaller in oxygen than in nitrogen, so we must suppose that the same effect occurs in nitrogen; but this is not the case. Therefore, we suppose either a formation of semi-valence molecules in connection with the paramagnetism, or a deformation of the infra-molecular bands under the influence of the magnetic field of the neighbouring molecules.

Professor J. Errera (*a*) in reply to Mr. C. R. Bailey, communicates: I have already referred to (1) the interpretation of the bands as due to intermolecular forces. (2) As to the experiments of Dr. Mollet, we do not at all agree with Mr. Bailey, because the two papers quoted (Maione and Kinsey and Ellis) are not at all in disagreement with our results. In fact, Maione did not work at sufficiently low concentrations to obtain the band at 2·73 μ. In pure alcohols or in concentrated solutions this band is masked by the much stronger 3 μ band. His lowest concentration was 4·3 mol./lit. in benzene and the band begins to appear clearly only at a concentration of 0·33 mol./lit. in CCl_4. Kinsey and Ellis, working on a harmonic of our band, find for the dilute solutions, in addition to the broad O—H band, a sharp one at smaller wave-length which appears also in the vapour state. In an earlier paper [18] we have observed, too, that the O—H band in the 1·5 μ region is complex, and that the two individual components change with temperature, in a way that is very similar to the results found for the bands at 3 μ. (*b*) In reply to Dr. E. Bartholomé: We have found in recent experiments with Dr. Mollet, a strong band at 2·73 μ, also in the C_2H_5OH vapour (80° C., ~ 760 mm.), in complete confirmation of our point of view.

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[18] H. M. Bloch and J. Errera, *J. Physique*, 1935, 6, 154.

PART II. STRUCTURE AND MOLECULAR FORCES IN SOLUTIONS.

INTERMOLECULAR FORCES IN SOLUTIONS

(Introductory Paper).

By Joel H. Hildebrand

Received 19*th September*, 1936.

It is a source of satisfaction to one who has long been cultivating the field comprehended in the title of this symposium to find it almost suddenly becoming popular and yielding a sufficient harvest of results to claim the attention of this distinguished society. That the simpler problems of the gaseous state, on the one hand, and of the solid state, on the other, should receive prior attention was to be expected, but those of the liquid state could not be indefinitely neglected. Simpler problems are attractive for their promise of prompt and spectacular results, but complicated problems usually present the greater challenge. A number of competent discoverers are finding this particular challenge attractive and the region is no longer deserted.

Progress has been delayed, until rather recently, by over-simplification of the problem. For example, the equations for van der Waals liquids were attractive for their simple algebra and, with the prevailing avoidance of quantitative tests, gave the impression that the problem was largely solved. Again, the formal analogy between gas pressure and osmotic pressure made the behaviour of dilute solutions so easy to treat that we were almost convinced that the rôle of the solvent was simply to supply space for a sort of gasified solute. Having been started wrong in our youth, it has been hard for us to realise that the solute and the solvent are co-ordinate components, at least for molecules with the same types of field, and that a set of equations is not likely to be correct unless they are symmetrical with respect to both components.

Then again, experimental data that seemed to give evidence in favour of simple relations too often did so because the substances chosen did not represent sufficiently drastic variations of crucial factors. The effects of molecular field type and strength, of molecular size and shape, have too rarely been studied one at a time. We are now, fortunately, beginning to see an accumulation of critically selected material, of which our program presents some notable examples.

If I understand my function correctly, it is not to abstract for you the papers to be presented—that will be done by the authors themselves—but rather to lend coherence to the program; by helping its parts to stick together, by emphasising its relation to the past, and by hazarding a few glances toward the future, pointing to leads for investigation that appear promising. I believe I may assume that most of that to which I shall refer is already familiar in some detail, and that I need give only a certain large scale view.

I wish to emphasise, first, the importance of recognising the different contributions possible to the total intermolecular field. These include at least the following: first, the potential between charged ions; second, the potential between permanent electric dipoles; third, the potential between a permanent dipole and the temporary dipole it may induce in another molecule; fourth, the potential of actual chemical or electron pair bonds that may be formed; fifth, the potential due to the interaction always occurring between electron systems, regardless of the presence or absence of the previously mentioned effects. We have been fortunate, indeed, in having a contribution on this subject from Professor London, to whom we owe the theory of this effect. The ambiguity attaching to the usual term, van der Waals forces, might well be removed by speaking, instead, of London forces. Progress has been made in the theory of each of the foregoing effects, and their relative strengths can be at least roughly determined in favourable cases. We are emerging gradually from the period in which enthusiasts have overworked one type of intermolecular field to the neglect of others also present. No longer is it permissible to neglect the electron interaction in dealing with assemblages of ions or of polar molecules. This point needs still to be emphasised; for the London effect may far outweigh the dipole effect, even in the case of rather strong dipoles. It may also tend to produce different arrangements. For example, the dipoles of two molecules of ethyl iodide, having a strength of $1 \cdot 7 \times 10^{-18}$ e.s.u, would tend to force an antiparallel arrangement; however, the iodide atoms, which would have a London attraction for each other far greater than for the ethyl groups, would tend to force a parallel arrangement. Again, only through a consideration of the magnitude of the London forces can we see an explanation of the fact that many species of polar molecules show little or no evidences of association in solutions with non-polar molecules. Sulfur, iodine and stannic iodide dissolve almost equally well and to give regular solutions both in carbon tetrachloride, with zero moment, and in chloroform, with a moment of $1 \cdot 1 \times 10^{-18}$ e.s.u. The electric moment of the latter appears to enhance its molecular field slightly without causing specific interactions.

It is becoming evident, again, that the term "association," under which we have lumped all departures from normal behaviour, must be subdivided into association arising from the interaction of dipoles, and that due to the formation of definite chemical bonds. Of these, perhaps the most interesting are the hydrogen bonds, or "bridges" between oxygen, nitrogen or fluoride atoms, a species of chemical interaction. Substances containing hydroxyl, carboxyl or amino groups show a type of association markedly different from that of most other dipoles, such as those due to halogens.

Systematic and thorough studies of this effect, such as the ones to be presented by Butler, and by Glasstone, are very important. The biochemist should profit particularly by the comprehensive investigation of the strength of the hydrogen bonds between hydroxyl, carboxyl and amino groups, for the proteins are bound together largely through these groups.

Most of the possible combinations of molecular field types appear to deserve more attention than they have yet received. The following appear particularly inviting. First, interionic forces, as in fused salt solutions, including both strong and weak salts. Second, forces between ions and polar molecules, getting farther into the realm of concentrated solutions. It may prove illuminating in this connection to cut loose from the infinitely dilute solution as the standard state of reference for activity coefficients, particularly when comparing different solvents, where the usual definition provides no common ground for comparison. Thirdly may be mentioned systems containing two different polar species, which constitute the vast majority of those which organic chemistry has to offer. Several of the contributions to our programme have to do with such systems.

Too often, in the past, the components of solutions have been poorly chosen to differentiate these various contributions to molecular fields. We still need more data on the effect of variation in the strength of the London field through the study of systems of symmetrical non-polar molecules. Such substances as phosphorus, the tetrahalides and the hydrocarbons present many systems not yet investigated, among which the field strength varies enormously. The solutions of non-polar gases are also significant in this connection, and it is unfortunate that published figures for solubility are often so discordant as to appear utterly unreliable. Accurate determinations of gas solubilities are much to be desired.

Studies of the structure of both pure liquids and solutions are essential in bridging the gap between the potential of the entire liquid mass and the potential between molecular pairs. A good beginning has been made, and we are fortunate in having further contributions upon our programme. The magnitude of the potential between molecular pairs can be calculated for pure liquids by the aid of the structure as revealed by X-rays, which accords well, for symmetrical fields, with the random distribution which thermal agitation would lead us to expect. In the case of solutions, however, the intermolecular potentials and the structure do not appear as easily separable factors, and each presents at present some interesting unsolved problems. A high potential between the molecules of one species undoubtedly tends to produce clustering and eventual separation of that species as a separate phase. This affects the structure of the solution in such a way as to introduce great uncertainty into the resolution of the potential of the entire mass of the solution into potentials between like and unlike pairs of molecules.

There is room for further attacks upon the problem of structure by both experimental and theoretical methods. X-rays have been applied to a few pure liquids with sufficient rigour, *i.e.*, taking account of all the elements of scattering, to give reliable information concerning their structure. Similar studies are called for upon solutions. The obvious complications can be reduced by a judicious selection of substances whose atoms present wide variations in scattering power. Here again the tetrahalides offer particularly interesting possibilities, *e.g.*, carbon tetrachloride and stannic iodide.

It would appear desirable to bear in mind the classification of molecular fields previously referred to in the selection of systems for investigation. We may expect different structures in solutions wherein the clustering or association arises from different causes, *e.g.*, mere difference in non-polar field strength, as with silicon chloride-stannic iodide ; dipole association, as with chlorobenzene-hexane ; hydrogen bond formation to yield definite dimers, as with acetic acid in benzene, or indefinite aggregates, as with the alcohols in hexane. It should be obvious that conclusions drawn from one or these types cannot be extended blindly to the others.

The application of theoretical statistical methods to the structures and potentials of solutions is to be seen particularly in the noteworthy studies of Guggenheim, of Kirkwood, and of Eyring. The problem of deriving mathematically the probability function as used by Prins, Zernike, Debye and Menke, for the structure of a pure liquid is one from which all mathematicians to whom I have broached the subject have so far retreated. I mention it, however, because it seems to be the kind of problem that ought to be soluble. The problem presented by solutions of molecules of different sizes and shapes is, of course, vastly more difficult. Most of us would tackle the statistical problems that could be presented by arrangements of checkers on an ordinary checkerboard with some hope for success, but we would shy off with dismay from a game such as might be played in Wonderland with pieces of varying shapes and sizes on a board whose squares would change sizes to accommodate the pieces. It would seem, however, that some future Lewis Carroll should arise mathematician enough to train an Alice to play such a game. Meanwhile it is quite fair, of course, to simplify the problem, as Guggenheim has done, by considering molecules of equal sizes.

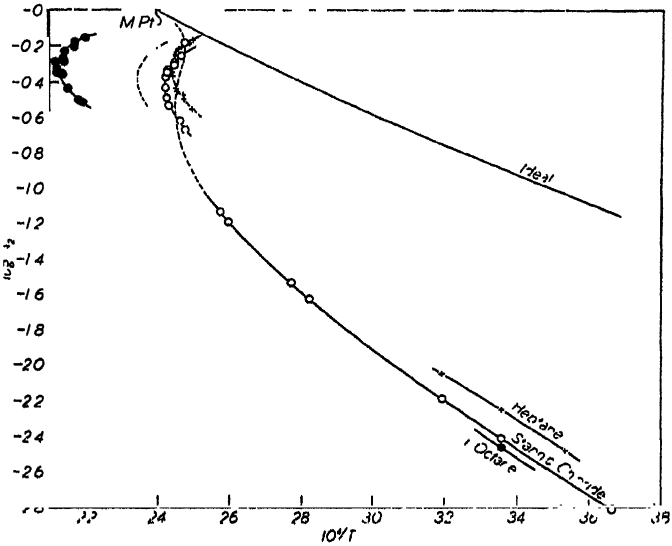

Fig. 1. -Solubility of Stannic Iodide.

A certain amount of light is thrown upon the problem by studies of the entropy of mixing. We have come to recognise a large number of systems whose behaviour has been designated as "regular," *i.e.*, the entropy of mixing is approximately the same as for an ideal solution of the same composition. This situation is readily detected either by comparing the heat of mixing with the free energy of mixing or by examining the temperature coefficient of the latter. The ordinary statistical interpretation of entropy suggests that within the limits to which a solution behaves regularly the thermal agitation is sufficient to insure randomness of mixing. It must be recognised, of course, that unequal molecular fields always tend to produce segregation, and that no such system could be completely regular at all temperatures and compositions. Segregation into two liquid phases must always ensue when the temperature is sufficiently lowered, provided a solid phase does not intervene. The difference between the points of view that have been expressed by

Guggenheim, on the one hand, and by Scatchard and myself on the other, is largely one of emphasis. Guggenheim has directed attention to the reality of the clustering effect; we have separately expressed our satisfaction that its neglect yields no more serious discrepancies than it does in actual calculations.

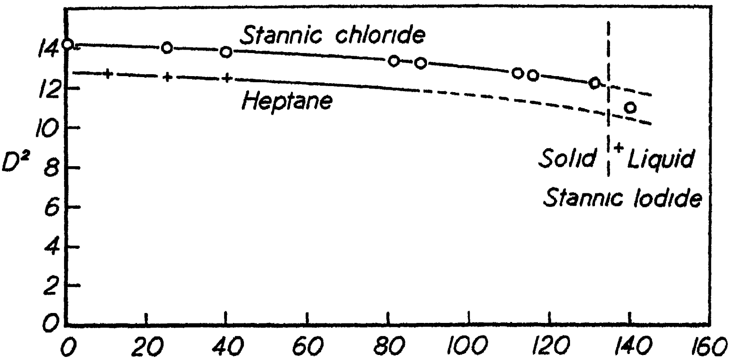

FIG. 2.—Effect of temperature on deviations for Stannic Iodide solutions.

One of my students, Dr. George R. Negishi, has obtained experimental material that seems to offer an excellent check on theories of this effect. He has measured the solubility of stannic iodide in silicon chloride through a long range, from 0° to 139°, embracing both the solid-liquid and the liquid-liquid systems. Fig. 1 shows these data, together with the less complete data for stannic iodide in normal heptane and in iso-octane (2, 2, 4-trimethyl pentane). We will examine these results to learn to what extent the course of the curve for the solubility of solid stannic iodide at lower temperatures suffices to account for the position of the curve for the liquid-liquid system. We may use the approximation equation, $4\cdot575T \log (a_2/N_2) = v_1V_2^2D^2$, applicable to regular solutions. Here N_2 is the solubility of stannic iodide expressed in mole fraction; a_2 is its activity referred to the pure liquid state; for the solid form it equals N_2', the ideal solubility, derived from its melting-point and heat of fusion; v_1 is the molal volume of silicon chloride and D the difference between the square roots of the energy of vaporisation per c.c. of the two components in the liquid form. V_2 is the volume fraction of stannic iodide. If the equation were strictly applicable, D^2, which most simply expresses the deviation of the system from ideal behaviour, should be constant throughout the entire range. Calculating D^2 from the data themselves, we see that it falls off slowly with temperature, as shown by the figures in Table I., which are graphically set forth in Fig. 2, together with similar ones in heptane solution.

TABLE I.—TREND OF DEVIATION WITH TEMPERATURE. SnI_4 IN $SiCl_4$.

t° C.	D^2.	
0	14·2	Solid SnI_4
25	14·0	
40	13·8	
81	13·3	
88	13·1	
112	12·6	
116	12·5	
131	12·2	
140	10·9	Liquid SnI_4

There is also a drop in the value of D^2 for both systems in going to the critical liquid-liquid solution point which throws the calculated critical temperature off by an amount indicated in Fig. 1. The formula is very sensitive in this region so that a small change in D corresponds to a large shift in critical temperature.

The formula takes no account of clustering and it is rather surprising that it holds as well as it does, which is encouraging for purely practical purposes. The trend in D^2 with temperature at lower temperatures is due to other shortcomings of the formula, for clustering evidently assumes importance only in the immediate neighbourhood of the critical temperature and composition. The studies of Krishnan of the scattering of light furnish direct evidence of this.

One may infer from the extremely rapid falling off of opalescence with departure from the critical solution temperature that clustering may be expected to exert a considerable effect upon the shape of the liquid-liquid solubility curve near its maximum, but to be comparatively unimportant elsewhere.

When the structure of a solution is known it is possible to distribute the intermolecular potentials between the like and the unlike molecules and thus attack the crucial problem of the relation of the latter to the former. Dispersion theory, at present, says that the potential between unlike molecules is equal to or less than the geometric mean between the intermolecular potentials of the like molecules; how much less cannot be stated. The complicated interactions between two different electron systems may be a long time in yielding to complete theoretical treatment, so we may rely upon experiment. An ideal attack is the direct observation of the interaction between the paths of single pairs of molecules in molecular beams.

Pending the accumulation of data by this direct method we may draw certain tentative conclusions from the behaviour of liquid mixtures. The general equation derived by myself and Wood has been reduced to an approximate but workable form by invoking certain assumptions, including the geometric mean for potentials as just stated. The deviation of a solution from ideal behaviour, according to the resulting approximate equation, depends upon the magnitude of the difference between the square roots of the energies of vaporisation per c.c., the internal pressure or the "energy density," as Scatchard has called it. Cases where the deviation from ideal behaviour is greater than this equation indicates may be interpreted, if we place all the blame upon one factor alone, as indicating that the potentia between the unlike molecules is less than the geometric mean. This seems to be generally the case, as seen from the accompanying figures. It will be interesting to ascertain through more extensive study, and preferably by applying the more accurate equation, whether the departure follows any general rules or is dependent

TABLE II.—COMPARISON OF VALUES OF D CALCULATED FROM INTERNAL PRESSURES WITH THOSE DETERMINED DIRECTLY FROM THE SOLUTIONS.

System.	D Determined from	
	Int. Pies.	Solubility.
$C_6H_6-C_4H_{10}$	2·4	2·6
C_6H [illegible]	1·0	1·5
$C_6H_6-CS_2$	1·0	1·8
CCl_4-Br_2	3·1	2·8
CCl_4-SiCl_4	1·0	1·1
$CCl_4-C_6H_6$	0·6	1·0
$CCl_4-nC_7H_{16}$	1·1	1·5
$SiCl_4-SnI_4$	1·8	3·7
$C_6H_6-P_4$	5·0	5·7
$SiCl_4-I_2$	6·0	6·1

rather on the particular types of electron systems involved. The figures compared in Table II. include some uncertainty regarding the energies of vaporisation at 25°. This may be circumvented by using a triangle of the three binary systems of the same three components and see whether the deviation for one is given additively by the deviations of the other two. The systems set out in Table III. yield evidence of this sort.

TABLE III.—TEST OF ADDITIVITY OF DEVIATIONS FROM IDEALITY.

Components.			D_{13}.	D_{23}.	D_{12}.	
1.	2.	3.			Calc.	Obs.
C_6H_6	CCl_4	C_7H_{16}	2·50	1·51	0·96	0·95
C_6H_6	CCl_4	CS_2	2·70	1·90	0·71	
$SiCl_4$	I_2	CCl_4	0·88	5·45	0·33	0·14
$SiCl_4$	SnI_4	CCl_4	0·88	3·02	3·90	3·76

The agreement is evidently good, though far from perfect.

In most of the simplified treatments heretofore used for dealing with intermolecular potentials the centre of the molecule is taken as the measure of intermolecular distance and corresponding potential. The question suggests itself whether it would not be better to consider the atoms as the attracting centres. The range of attraction is so short, falling off as it evidently does with the sixth power of the distance, that the adjacent atoms contribute most of the intermolecular potential. The tetrahalides, again, can furnish excellent material for analysis on this basis.

Effects of differing molecular sizes and shapes present some interesting questions. Several of my students have been measuring the solubility of dicetyl, normal dotriacontane, in a number of solvents. The molecules of this substance depart greatly from the more or less spherical shape of molecules of most of the substances that have justly claimed first attention. They are probably linear in the solid, although they may be more or less coiled in the liquid and vapour. The proper quantitative treatment of these observations awaits information concerning the heat of a transition observed by Dr. W. F. Seyer, of the University of British Columbia, of which I have learned through a private communication. Meanwhile, however, one significant observation is possible. Seyer has measured the solubility of dicetyl in butane, and Wachter, under my direction, has measured the solubility in heptane. The solubilities in the two cases are nearly identical, when expressed in mole fractions, and appear to conform closely to Raoult's law. Now one might conclude superficially that the escaping tendency of a hydrocarbon molecule would be nearly the same regardless of whether it is surrounded by a certain number of octane molecules or twice as many butane molecules, *i.e.*, the volume concentration, not the mole fraction, would be determinative. That this is not the case and that ideal solutions result from mixing molecules of such different dimensions appears to be an important experimental fact.

The observation just made is an excellent illustration of the abundant opportunities for discovery presented by this field. Solutions have been under investigation for many years, and yet we have to seize upon an almost isolated piece of experimental support for the very foundation of solution theory, *i.e.*, Raoult's law. Guggenheim will very appropriately direct our attention to the uncertainty under which we labour regarding the basis of this law.

Before closing I would like to remind you that metallic solutions offer a considerable amount of unexplored territory. The studies thus far made indicate that the potentials between unlike molecules of metals are more complicated functions of those between the like molecules than is the case with non-metallic, non-polar molecules. At the same time, the use of electromotive force to measure the partial molal free energies has already put at our disposal a considerable body of data which invite better theoretical treatment than they have yet received.

Finally, I will venture to predict that, if another symposium on this topic is held between five and ten years hence, the subject will have advanced sufficiently to permit predictions of solubility for solutions of various types with a fair degree of accuracy, say 10 per cent. However, before the error shall have been reduced to 1 per cent., much more time and labour will be demanded. The field will, therefore, not be worked out for a long time. The main features of the problem are still before rather than behind us, and the finer points stretch off into the distance.

THE THEORETICAL BASIS OF RAOULT'S LAW.

By E. A. Guggenheim, M.A.

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The foundations of the thermodynamics of ideal solutions were laid by van t'Hoff, but his treatment and formulæ are applicable only to extremely dilute solutions.[1] Although this restriction was realised by van t'Hoff himself, his laws have often been misapplied by later authors to concentrated solutions. In particular his osmotic pressure formula which has the same form as the formula for the pressure of a perfect gas is even now regarded by some writers as an accurate law, although at very high concentration of the solute it becomes absurd, since it gives a finite value for the osmotic pressure in the limiting case of pure solute. The accurate expressions of the ideal laws applicable to solutions of any concentration were first given by van Laar,[2] but his formulation of them was unnecessarily complicated. Their simple formulation is due to G. N. Lewis [3] and to Washburn.[4] These ideal laws can, of course, be express'ed in various forms thermodynamically equivalent to one another. The simplest statement of these laws is that each species in a perfect or ideal solution obeys Raoult's law in the form : partial vapour pressure/mole fraction is constant at constant temperature and external pressure. For a binary mixture containing n_1 moles of the species 1, and n_2 moles of the species 2, the conditions that it should be perfect are then

$$p_1 = p_1^0 n_1/(n_1 + n_2) \qquad . \quad . \quad . \quad 1.1$$

$$p_2 = p_2^0 n_2/(n_1 + n_2) \qquad . \quad . \quad . \quad 1{\cdot}2$$

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[1] van't Hoff, *Z. physikal. Chem.*, 1887, **1**, 480.

[2] van Laar, *ibid.*, 1894, **15**, 457.

[3] Lewis, G. N., *J. Am. Chem. Soc.*, 1908, **30**, 668.

[4] Washburn, *Z. physikal. Chem.*, 1910, **74**, 385.

where p_1, p_2 denote the partial vapour pressures in the mixture and p_1^0, p_2^0 denote the vapour pressures of the pure substances at the same temperature and external pressure. From (1.1), (1.2) it is easy to deduce that the two species mix in all proportions at constant temperature and pressure without any heat effect or volume change. But the converse is not true. The problem we want to discuss is the following: if two species mix in all proportions at constant temperature and pressure without heat effect or volume change, what further conditions is necessary for mixtures to be perfect? We might hope to obtain an answer by means of statistical mechanics or thermodynamics or experiment. Actually the final answer is still unknown.

The application of statistical mechanics to the problem requires the use of some simple model for the molecules. The laws of perfect solutions have been deduced for a model of spherical molecules of approximately the same size; actually the sizes of the two species must be assumed sufficiently alike so that each molecule of either species is directly surrounded by the same number of other molecules.[5] Up to the present no one has succeeded in applying statistical mechanics to a more general model

The thermodynamic method of attack gives no definite answer, but it is of value in showing the type of law that might be obeyed by mixtures of molecules of different sizes. Let us denote by G the Gibbs function (or Gibbsian free energy) for a mixture of n_1 molecules of the species 1 and n_2 molecules of the species 2 at the temperature T and the pressure P and by G_1^0, G_2^0 the Gibbs functions for one mole of each of the two pure species at the same temperature and pressure. Let us further define a function $\phi(T, P, n_1, n_2)$ by the relation

$$G - n_1G_1^0 - n_2G_2^0 = RT\left\{n_1 \log \frac{n_1}{n_1+n_2} + n_2 \log \frac{n_2}{n_1+n_2} + \phi(T, P, n_1, n_2)\right\}. \quad 2.1$$

Then it is easily shown that, if the two species mix in all proportions at constant temperature and pressure without any heat effect, ϕ is independent of T; similarly, if they mix without volume change, ϕ is independent of P. For the type of mixtures that we are interested in, we may therefore write $\phi(n_1, n_2)$ instead of $\phi(T, P, n_1, n_2)$. Moreover $\phi(n_1, n_2)$ must be homogeneous of the first degree in n_1, n_2. This is all that can be deduced from thermodynamics alone. From (2) we deduce for the partial vapour pressures the formulæ:

$$p_1 = p_1^0 \frac{n_1}{n_1+n_2} \exp\left(\frac{\partial\phi}{\partial n_1}\right), \quad . \quad . \quad . \quad 3.1$$

$$p_2 = p_2^0 \frac{n_2}{n_1+n_2} \exp\left(\frac{\partial\phi}{\partial n_2}\right). \quad . \quad . \quad . \quad 3.2$$

But we know that Raoult's law (1.1) must be obeyed by species 1 in the limit that $n_2/n_1 \rightarrow 0$ and Raoult's law (1.2) must be obeyed by species 2 in the limit that $n_1/n_2 \rightarrow 0$. To satisfy these conditions it is necessary that $\phi \rightarrow 0$ both when $n_2/n_1 \rightarrow 0$ and when $n_1/n_2 \rightarrow 0$. If we assume that $\phi(n_1, n_2)$ is a smooth function of the simplest possible kind, we can express it as a series of the form

$$\phi(n_1, n_2) = \frac{n_1n_2}{n_1+n_2}\left\{A_0 + A_1\frac{n_1-n_2}{n_1+n_2} + A_2\left(\frac{n_1-n_2}{n_1+n_2}\right)^2 + \dots + A_r\left(\frac{n_1-n_2}{n_1+n_2}\right)^r + \dots\right\}. \quad 4.1$$

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[5] Guggenheim, *Proc. Roy. Soc.*, *A*, 1932, **135**, 181; *Proc. Roy. Soc.*, *A*, 1935, **148**, 304.

This form of series is more symmetrical with respect to the two component species than the power series in $n_2/(n_1 + n_2)$ used by van Laar. From (4) we deduce

$$\frac{\partial\phi}{\partial n_1} = \left(\frac{n_2}{n_1 + n_2}\right)^2 \left\{A_0 + A_1\frac{3n_1 - n_2}{n_1 - n_2}\,\frac{n_1 - n_2}{n_1 + n_2} + A_2\frac{5n_1 - n_2}{n_1 - n_2}\left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2 + \ldots \right.$$
$$\left. + A_r\frac{(2r + 1)n_1 - n_2}{n_1 - n_2}\left(\frac{n_1 - n_2}{n_1 - n_2}\right)^r + \ldots\right\}, \qquad 5.1$$

$$\frac{\partial\phi}{\partial n_2} = \left(\frac{n_1}{n_1 + n_2}\right)^2 \left\{A_0 + A_1\frac{n_1 - 3n_2}{n_1 - n_2}\,\frac{n_1 - n_2}{n_1 + n_2} + A_2\frac{n_1 - 5n_2}{n_1 - n_2}\left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2 + \ldots \right.$$
$$\left. + A_r\frac{n_1 - (2r + 1)n_2}{n_1 - n_2}\left(\frac{n_1 - n_2}{n_1 + n_2}\right)^r + \ldots\right\}. \qquad 5.2$$

The number of terms required in these series will be determined by the accuracy aimed at and for most purposes two terms will be sufficient. We shall therefore set A_2, A_3, etc., equal to zero. The formulæ then reduce to

$$\phi(n_1, n_2) = \frac{n_1 n_2}{n_1 + n_2}\,\frac{(A_0 + A_1)n_1 + (A_0 - A_1)n_2}{n_1 + n_2} \quad . \quad . \quad 6.1$$

$$\frac{\partial\phi}{\partial n_1} = \left(\frac{n_2}{n_1 + n_2}\right)^2 \frac{(A_0 + 3A_1)n_1 + (A_0 - A_1)n_2}{n_1 + n_2} \quad . \quad . \quad 6.2$$

$$\frac{\partial\phi}{\partial n_2} = \left(\frac{n_1}{n_1 + n_2}\right)^2 \frac{(A_0 + A_1)n_1 + (A_0 - 3A_1)n_2}{n_1 + n_2} \quad . \quad . \quad 6.3$$

$$p_1 = p_1^0\frac{n_1}{n_1 + n_2}\exp\left\{\left(\frac{n_2}{n_1 + n_2}\right)^2 \frac{(A_0 + 3A_1)n_1 + (A_0 - A_1)n_2}{n_1 + n_2}\right\}, \quad 7.1$$

$$p_2 = p_2^0\frac{n_2}{n_1 + n_2}\exp\left\{\left(\frac{n_1}{n_1 + n_2}\right)^2 \frac{(A_0 + A_1)n_1 + (A_0 - 3A_1)n_2}{n_1 + n_2}\right\}. \quad 7.2$$

The question remains: what values might A_0 and A_1 reasonably have? If the species 1 and 2 have identical sizes and shapes then A_0 and A_1 may safely be assumed equal to zero. Hildebrand[6] reasons from this that the values of A_1 and A_2 will always be zero. (It must be remembered that we are considering only pairs of substances such as mix without heat effect or volume change.) But there is no obvious reason why A_0, A_1 should not be determined by the ratio of the volumes of the two molecular species, becoming zero in the special case that this ratio is unity. Suppose, for instance, we tentatively set

$$A_0 = \frac{(V_2 - V_1)^2}{4V_1V_2}, \quad . \quad . \quad . \quad . \quad 8.1$$

$$A_1 = \frac{V_2^2 - V_1^2}{12V_1V_2}, \quad . \quad . \quad . \quad . \quad 8.2$$

where V_1, V_2 are the molar volumes of the two species at the same temperature and pressure. (If the two species have different coefficients of thermal expansion or different compressibilities, these values of A_0 and A_1 will not be absolutely independent of temperature and pressure, but the deviation from constancy may be neglected for ordinary variations of temperature and presssure.) With these values for A_0, A_1 we have

$$A_0 + A_1 = \frac{(V_2 - V_1)(2V_2 - V_1)}{6V_1V_2} \quad . \quad . \quad . \quad 9.1$$

$$A_0 - A_1 = \frac{(V_1 - V_2)(2V_1 - V_2)}{6V_1V_2} \quad . \quad . \quad . \quad 9.2$$

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[6] Hildebrand, *Solubility*, Reinhold Publishing Corporation, 1936, p 20.

$$A_0 + 3A_1 = \frac{V_2 - V_1}{2V_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad 9.3$$

$$A_0 - 3A_1 = \frac{V_1 - V_2}{2V_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad 9.4$$

Our formulæ (7.1), (7.2) for p_1, p_2 become

$$p_1 = p_1^0 \frac{n_1}{n_1 + n_2} \exp \left\{ \left(\frac{n_2}{n_1 + n_2} \right)^2 \frac{V_2 - V_1}{2V_1} \cdot \frac{n_1 3V_2 + n_2(V_2 - 2V_1)}{(n_1 + n_2)3V_2} \right\} \quad 10.1$$

$$p_2 = p_2^0 \frac{n_2}{n_1 + n_2} \exp \left\{ \left(\frac{n_1}{n_1 + n_2} \right)^2 \frac{V_1 - V_2}{2V_2} \cdot \frac{n_1(V_1 - 2V_2) + n_2 3V_1}{(n_1 + n_2)3V_1} \right\} \quad 10.2$$

These rather unattractive formulæ can be transformed into simple forms when the species in question is dilute. Thus when $n_1 \ll n_2$ formula (10.1) becomes correct to terms in $(n_1/n_1 + n_2)^2$ and neglecting terms in $(n_1/n_1 + n_2)^3$,

$$p_1 = p_1^0 \frac{n_1}{n_1 + n_2} \exp \left\{ \frac{(V_2 - V_1)(V_2 - 2V_1)}{6V_1 V_2} - \frac{n_1}{n_1 + n_2} \frac{V_1 - V_2}{V_2} \right\} \quad 11.1$$

which can be written in the alternative form, correct to terms in $(n_1/n_1 + n_2)^2$,

$$p_1 = k_1 \frac{n_1}{n_1 V_1 + n_2 V_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad 12.1$$

where
$$k_1 = p_1^0 V_2 \exp \left\{ \frac{(V_2 - V_1)(V_2 - 2V_1)}{6V_1 V_2} \right\} \quad . \quad . \quad 13.1$$

Similarly when $n_2 \ll n_1$ formula (10.2) is, correct to terms in $(n_2/n_1 + n_2)^2$, equivalent to

$$p_2 = k_2 \frac{n_2}{n_1 V_1 + n_2 V_2}, \quad . \quad . \quad . \quad . \quad 12.2$$

where
$$k_2 = p_2^0 V_1 \exp \left\{ \frac{(V_1 - V_2)(V_1 - 2V_2)}{6V_1 V_2} \right\}. \quad . \quad . \quad 13.2$$

We see then that our particular choice of values for A_0, A_1 leads to Henry's law for the dilute component in the form: partial pressure of dilute component directly proportional to its volume concentration. *A priori*, there is no obvious theoretical reason why in dilute solution (12.1), (12.2) should be more or less accurate than (1.1), (1.2) and therefore the values (8.1), (8.2) chosen for A_0, A_1 are not obviously less reasonable than the value zero usually assumed. That the values of A_0, A_1 should be zero, is the simplest possible assumption, but it is only one amongst other possible assumptions.

The deviation between formulæ (10.1), (10.2) on the one hand and formulæ (1.1), (1.2) on the other are measured by the exponentials which we may call activity coefficients and denote accordingly by f_1, f_2; thus

$$f_1 = \exp \left\{ \left(\frac{n_2}{n_1 + n_2} \right)^2 \frac{V_2 - V_1}{2V_1} \cdot \frac{n_1 3V_2 + n_2(V_2 - 2V_1)}{(n_1 + n_2)3V_2} \right\}. \quad . \quad 14.1$$

$$f_2 = \exp \left\{ \left(\frac{n_1}{n_1 + n_2} \right)^2 \frac{V_1 - V_2}{2V_2} \cdot \frac{n_1(V_1 - 2V_2) + n_2 3V_1}{(n_1 + n_2)3V_1} \right\}. \quad . \quad 14.2$$

We give a table of values of f_1, f_2 for various compositions taking the value of v_2/v_1 as 1·25. We see that the deviations of f_1, f_2 from unity are mostly less than 1 per cent. It follows that even if the true laws were of the form (10.1), (10.2), the usual formulæ (1.1), (1.2) would be a very good approximation provided the molecular volumes do not differ by more than 25 per cent. For greater differences in size we cannot predict anything.

TABLE OF f_1 AND f_2 FOR v_2/v_1 1·25.

$\frac{n_1}{n_1 + n_2}$.	$n_1 + n_2$.		f_2.
	0·900	0·992	0·9996
0·167	0·833	1·000	0·998
0·250	0·750	1·007	0·996
0·500	0·500	1·012	0·994
0·667	0·333	1·008	1·000
0·750	0·250	1·006	1·007
0·900	0·100	1·0001	1·028

In the absence of any definite answer to our question either from statistical mechanics or from thermodynamics there remains the test of experiment. It is well known that mixtures do exist which obey the laws of perfect solutions in the forms (1·1), (1·2). It is probably less widely realised how scanty are the experimental data. The only examples for which these laws have been accurately established are ethylene bromide + propylene bromide and benzene + ethylene chloride, both mixtures having been studied by von Zawidski.[7] The following mixtures were investigated by Young and Fortey:[8] chlorobenzene + bromobenzene, ethyl acetate + ethyl propionate, toluene + ethyl benzene, *n*-hexane + *n*-octane, benzene + toluene. They measured in each case the boiling-points of mixtures of molecular proportions 1 : 3, 1 : 1 and 3 : 1 at various pressures. By interpolation they obtained the total vapour pressures at given temperatures and compared these with the values computed according to the laws of perfect solutions. They found exact agreement for the mixture chlorobenzene + bromobenzene and small but definite deviations for all the other mixtures. It is to be noted that they obtained no data for the partial vapour pressures of the two constituents of the mixture. Measurements were made by Linebarger[9] on the mixtures benzene + chlorobenzene, benzene + bromobenzene, toluene + chlorobenzene, toluene + bromobenzene. Young and Fortey[10] referring to these measurements write: "The method employed by Linebarger does not appear to give good results with volatile liquids, and his observed vapour pressures differ somewhat widely from those of Lehfeldt and Zawidski." More recently Calingaert and Hitchcock[11] have studied the mixtures butane + pentane, butane + heptane, pentane + heptane. They did not measure the partial vapour pressures directly, but studied the pressure — volume — temperature relations and deduced therefrom the partial vapour pressures by a method both ingenious and theoretically sound, but of such a nature that a small error in the data (such as due to a trace of impurity) might lead to large errors in the final results of the computations. Their data extend only up to 20 per cent. of the lighter constituent for the first two mixtures and up to 35 per cent. in the third. For the mixtures butane + heptane they find agreement with Raoult's law in the form (1·1), (1·2), for the other two mixtures they find disagreement. Their partial pressure curves for the latter two mixtures cannot be correct as they contradict the Gibbs-Duhem-Margules relation. The only quantitative evidence referred to by Hildebrand[6] in support of Raoult's law is the single sentence, "It is worth noting that the system butane-heptane obeys Raoult's law very accurately" with a reference to Calingaert and Hitchcock. No mention is made of deviations found by the same authors for the systems butane + pentane and pentane + heptane, nor of the fact that the data extend only from 0 per cent. to 20 per cent. of butane.

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[7] von Zawidski, *Z. physikal. Chem.*, 1900, **35**, 128.

[8] Young, *J. Chem. Soc.*, 1902, **81**, 768; Young and Fortey, *ibid.*, 1903, **83**, 45.

[9] Linebarger, *J. Am. Chem. Soc.*, 1895, **17**, 615, 690 (Unfortunately I have not been able to obtain access to these papers.)

[10] Young and Fortey, *J. Chem. Soc.*, 1903, **83**, 63.

[11] Calingaert and Hitchcock, *J. Am. Chem. Soc.*, 1927, **49**, 750.

In short, the only reliable, accurate and direct evidence for partial vapour pressures of a binary mixture obeying the laws (1·1), (1·2), are von Zawidski's data for ethylene-bromide + propylene bromide and for benzene + ethylene chloride. The ratios of the molar volumes are for propylene bromide/ethylene bromide 104/86 = 1·21 and for ethylene chloride/benzene 94/89 = 1·06. Even for the former mixture the distinction between formulæ (1·1), (1·2), on the one hand and formulæ (10·1), (10·2), would be hardly detectable. The same applies to the mixtures studied by Young and Fortey. I think it would be of great interest to have data for mixtures such as benzene + diphenyl or benzene + triphenylbenzene and I am planning to make measurements on mixtures of this type.

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*GENERAL DISCUSSION.**

Professor J. Kendall (*Edinburgh*) said: While it is true that very few direct confirmations of Raoult's law have been obtained by the study of the partial vapour pressures of binary liquid mixtures, freezing-point depression and solubility investigations furnish a large number of examples of ideal systems. Reference may be made to Hildebrand, *Solubility*, Reinhold Publishing Corporation, 1936, and Timmermann's, *Les Solutions Concentrées*, Masson et Cie, 1936.

Dr. M. Magat (*Paris*) said: I would not exclude *a priori* every possibility of complex formation in organic compounds by the appearance of semi-valences or co-valences, between saturated molecules. I know of no case, however, where the van der Waals' forces hypothesis, if correctly applied, fails. In particular, dipole attraction can explain many more cases than is generally supposed if they are applied in conjunction with the special molecular form in each case, having regard to the position of the dipole or, often, the supposed multipoles. Thus, in the present case of ether and chloroform we stated, some years ago, that their individual "associations" are weak, because the dipole moments are situated relatively far inside the molecule. In other words, for steric reasons the dipole moments of two ether or two chloroform molecules cannot approach one another sufficiently. On the other hand, chloroform can "enter" into the ether molecule like a key into its hole. This explains the particularly strong associations in this case. The same applies in the case of acetone and chloroform. I believe that by applying this method in other cases we shall explain many phenomena. It is only when such explanation fails that we need to come back to 'semi-valences."

Dr. R. J. W. Le Fèvre (*London*) said: Professor Hildebrand has emphasised the point that molecules possessing quite strong dipoles may associate together in parallel rather than antiparallel alignment. We have found that the apparent variations of dipole moment of chloro- and nitrobenzenes, with the solvent in which measurement is effected, can be satisfactorily explained by assuming *both* kinds of association to be possible[12] Since the sides of these molecules present the greatest areas, a side-to-side (rather than edge-to-edge or random) orientation in the association complex (with the maximum number of atoms in the closest possible contact) is most probable. Complete formation of bimolecular units in which the dipoles have anti-parallel directions evidently does not occur, because the liquids in the pure state exhibit polarisations corresponding to moments of 1·2 and 1·7 D units respectively. Association complexes containing odd numbers of molecules have, therefore, been considered. For simplicity and as an example, we will mention here only the two extreme configurations which three molecules afford: (1) the chief dipoles of the participating molecules are in parallel alignment, and (2) they are arranged alternately. Whatever the configuration, however, each permanent dipole (μ) will cause the development of induced dipoles (μ') in the neighbouring molecules.

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* On the preceding two papers.

[12] Le Fèvre and Le Fèvre, *J.C.S.*, 1936, 487; Le Fèvre and Russell, *ibid*, 491.

The orientation polarisation of a unit volume of a liquid, originally containing n molecules but now having only $n/3$ groups will be, for (1) $\frac{4}{3} \cdot \frac{\pi n}{kT}(\mu - \mu')^2$ and for (2) $\frac{4\pi n}{27kT}(\mu + \mu')^2$.

The important question is, what values of μ' will make these expressions less than $\frac{4\pi n\mu^2}{9kT}$ (the true orientation polarisation for the separated molecules)? A calculation shows that values of μ' *greater* than 0·42 μ in (1) and *less* than 0·73 μ in (2) will suffice. Since such figures are not unlikely to occur in actual fact, both types of association may well be instrumental in the apparent alteration of the moment of a solute by its solvent. It may be added that, of course, no liquid or solution is imagined to be a static mixture of units such as these, but rather to be an average or equilibrium corresponding *in effect* to some configuration intermediate between them. Such a view seems more reasonable than to consider, as some workers have done, association of our second type alone.

Professor W. E. Garner (*Bristol*) (*communicated*). Professor Hildebrand mentioned that dicetyl showed anomalous solubility curves which he considered might be due to a transition in the solid state. The hydrocarbons C_{34}, C_{30}, C_{26} and C_{22} give rotating forms in equilibrium with the melt and pass over to tilted forms 4-7° C. below the melting-point. The following heats were obtained:—[13]

Atoms.	M.P. °C.	Heat of Crystn. of Vertical Form K. cal./mol.	Heat of Transition K. cal./mol.
22	43·8	11·7	6·90
26	56·1	14·04	8·37
30	65·5	16·45	8·72
34	72·4	19·11	11·48

The heats of crystallisation of the vertical forms are not very sensitive to impurity, but the heats of transition are very much affected. C_{26} and C_{34} were the purest of the four hydrocarbons and from these results it is estimated that the heat of transition for C_{32} hydrocarbon is approximately 10·7 K. cal./mol.

Dr. P. Gross (*Wien*) said: At what range of temperature, especially in relation to the critical temperatures, were the experiments with dicetyl carried out? How is the relation between the thermodynamic molecular volume and the actual need of space of a molecule, estimated in these cases, for instance, by X-ray data? I think this relation should be taken into consideration, particularly in cases where (more or less) free rotation is supposed to occur.

Professor J. H. Hildebrand (*Berkeley, Cal.*) said: I believe that Dr. Guggenheim has done us an important service in directing attention to this uncertainty, which ought not to be permitted to remain with us long. On the theoretical side, there is one sort of system that lends itself to statistical treatment, even if in rather artificial form, *i.e.*, a parallel arrangement of hydrocarbon chains of two different lengths. (The "mussed up" arrangement can hardly have a very different energy.) The energy of transfer of a molecule of one species from the solution to its own pure liquid would be practically zero, regardless of the relative lengths of the two species.

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[13] Cf. Garner, van Bibber, and King, *J.C.S.*, 1931, 1533.

Experimentally, the evidence does not appear to me to be as meagre as it appears to Dr. Guggenheim. It is true that we have few reliable investigations of vapour pressures over the whole range, but even if we had, the departures of the vapours from the ideal gas laws would make small departures from Raoult's law of uncertain significance. On the other hand, we have numerous instances of freezing-point or solubility curves which obey Raoult's law very closely, including many components of greatly differing volumes, such as naphthalene-chlorobenzene, sulphur-iodine, benzene-diphenyl, iodine-stannic iodide, cadmium-bismuth. The data may not cover the entire range of composition but, where the "solute" is ideal in dilute solution, it can hardly be expected to deviate as it becomes more concentrated. I am confident that a pure volume effect must be sought in fractions of a per cent.

Dr. A. Klinkenberg (*The Hague*) said: I should like to state a few particulars about the expansion in series of the function ϕ, or rather of its derivatives with respect to n_1 and n_2 which are the quantities in which we are actually interested.

It is said that: "The number of terms required in these series will be determined by the accuracy aimed at and for most purposes two terms will be sufficient."

It occurs to me that this statement is only justified when the series is convergent. Now the variable of the power series $\frac{n_1 - n_2}{n_1 + n_2}$ will be small for approximately equimolecular mixtures, but Dr. Guggenheim later uses these power series for $n_1 \ll n_2$ or $n_1 \gg n_2$, *i.e.*, for

$$\frac{n_1 - n_2}{n_1 + n_2} = + 1 \text{ or } - 1.$$

If no arguments exist in support of the assumption $A_2 = A_3 = \ldots = 0$ it follows that one might just as well have chosen any other combination of A values in order to obtain a function capable of representing certain observed facts. In particular, proportionality of partial pressure and volume concentration may just as well be obtained with other values of A_0. In my opinion, therefore, the particular values of A_0 and A_1 as given in equations 8·1 and 8·2 cannot be expected to have a physical meaning.

Dr. S. Glasstone (*Sheffield*) said: The apparent ideality of the benzene-ethylene dichloride system may possibly be due to the cancellation of deviations acting in opposite directions, much as is the case with the "pseudo-ideal" systems studied by Professor Kendall. In spite of the possibility of free rotation in ethylene dichloride, its dipole moment is almost the same in *n*-heptane, carbon disulphide, carbon tetrachloride, chloroform and ether solutions, the value being about 1·4 *D* at ordinary temperatures and increasing with increasing temperature. In benzene, however, the dipole moment is 1·77 *D* at room temperature, but it decreases slightly as the temperature is raised. Stearn and Smyth[14] suggested that benzene forms loose complexes with ethylene dichloride, and preliminary measurements of the dielectric polarisation of this system, performed in the Sheffield laboratories, show a distinctly abnormal behaviour.

Dr. P. Gross (*Wien*) said: The very thorough paper by Dr. Guggenheim[15] gives a more general answer to the question as to what conditions are necessary for solutions to be ideal. I do not believe that two liquids consisting of spherical molecules of very different sizes can mix without change of volume at a temperature range sufficiently far from the critical temperature; unless there is some model for such a mixture of which I am unaware.

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[14] *J. Amer. Chem. Soc.*, 1934, **56**, 1667.

[15] *Proc. Roy. Soc.*, 1935, **148**, 304.

What objections are there, if any, to the well known Planck—van der Waals transition[16] at constant temperature in a mixture of ideal gases, which would give for all concentrations $\phi = 0$ quite automatically. This method, of course, which leads the system through a series of unstable states, is nothing else but the introduction of the usual statistical mechanical interchange term (*Vertauschungsglied*).

Professor G. Scatchard (*Cambridge, Mass.*) (*communicated*): Further progress toward the solution of the problem proposed by Dr. Guggenheim may be made by combining statistical mechanics with his thermodynamic approach. If ϕ is independent of P, it must be the same in the liquid as in a gas of the same composition with P extremely small; but the simplest and surest result of statistical mechanics is that under these latter conditions ϕ is zero. Of course this argument does not exclude the possibility that, over a limited range of P and T, $\partial\phi/\partial T = 0$, $\partial\phi/\partial P = 0$, but $\phi \neq 0$, although it would be a remarkable coincidence if both derivatives were zero over the whole range of composition.

Mr. E. A. Guggenheim (*London*) said, in reply to Professor Kendall: Solubility and freezing-point measurements give only a single point at each temperature; also from such measurements, however accurate, it is extremely difficult to detect and measure small deviations from ideality, especially as one requires to know accurately not only the heat of fusion at one temperature, but also its temperature dependence. The data which I quoted were all that I could find covering a large range of concentrations at a constant temperature. There is no doubt that many two component systems obey the ideal laws roughly: the question raised is what are the conditions necessary for their exact validity. I agree with Professor Hildebrand that deviations due purely to a molar volume ratio different from unity are likely to be small, but no one knows how small. I do not believe they should be zero, as usually assumed.

In reply to Dr. Klinkenberg, I do not think the question of divergence occurs as I assume that we use a series with a finite number of terms. The more terms we use, the more accurate can we make the formula fit the physical curve. Of course, if we decide to improve the accuracy by adding a new term, we may have to revise the coefficients in the old terms. I agree with Dr. Klinkenberg that there is no physical basis for formulæ (8·1), (8·2); nor is there any for the usual assumption that all the coefficients A_0, A_1, A_2, . . . should be zero.

In reply to Dr. Gross, I cannot see any *a priori* reason why two liquids should be unable to mix without volume charge simply because their molecules are of different sizes. Planck's derivation of the laws of dilute solutions has been discussed and criticised by me elsewhere.[17] Essentially, Planck has to assume the system to have properties thermodynamically equivalent to those that he wishes to derive. In terms of a molecular model it is difficult to see what are the conditions for the validity of these assumptions.

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[16] Van der Waals, *Kohnstamm Thermodynamik*, p. 79; *Herzfelds Enzyklop. math. wiss.*, V., ii., 991.

[17] *J. Physic. Chem.*, 1930, 34, 1755.

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CHANGE OF VOLUME ON MIXING AND THE EQUATIONS FOR NON-ELECTROLYTE MIXTURES.

By George Scatchard.

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The approximate equations developed by the author,[1, 2, 3] for the properties of non-electrolyte mixtures have been found successful in many cases.[1, 4, 5, 6, 7]. The present paper extends the treatment to the volume change on mixing at constant pressure. Since it is necessary to use the assumption that the effect of this volume change on the free energy is negligible, we shall first outline the derivation to show how it depends upon this assumption, at the same time clarifying some points, and giving explicitly for the first time the equations for mixtures of more than two components.

For any system it is possible to write the total energy as

$$E = \Sigma_j N_j E_j^0 + \frac{\Sigma_j N_j \Sigma_k N_k \int \ldots \int \epsilon_{jkx} p_{jkx} \mathrm{d}x_1 \ldots \mathrm{d}x_6}{V},$$

in which the multiple integral is to be taken over all possible values of the six co-ordinates, $x_1 \ldots x_6$, which determine the relative position and orientations of a j and a k molecule,* for example the distance between two points, one fixed in each molecule, and the five angles which determine their relative orientations; N_j is the number of moles of the j'th species in the system; E_j^0 is the molal energy of the j'th species in the perfect gas state at the same temperature, and is a function of the temperature only; ϵ_{jkx} is Avogadro's number squared times half the mutual energy of two molecules of the j'th and k'th species at a specified value of each of the six co-ordinates; and p_{jkx} is the probability of each of the co-ordinates having its specified value.

We consider the change from an initial state in which the components are separated and are all at the same temperature T and pressure P_0 and the volume occupied by the j'th species is $N_j V_j$, to one of two final states, in each of which the components are mixed and the temperature is T. In the first final state the volume is $V_0 = \Sigma_j N_j V_j$, and the pressure is P; in the second final state the pressure is P_0 and the volume is $V_0 + V^M$. We shall designate the increment in any property with a superscript

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[1] G. Scatchard, *Chem. Rev.*, 1931, 8, 321.

[2] G. Scatchard, *Kemisk Maanedsblad* (*Copenhagen*), 1932, 13, 77.

[3] G. Scatchard, *J. Am. Chem. Soc.*, 1934, 56, 995.

[4] *Ibid.*, 1931, 53, 3186.

[5] J. H. Hildebrand and S. E. Wood, *J. Chem. Physics*, 1933, 1, 817.

[6] J. H. Hildebrand, *J. Am. Chem. Soc.*, 1935, 57, 866.

[7] J. H. Hildebrand, *Solubility*, Reinhold, N.Y., 1936.

* If the molecules are not rigid it will be necessary to treat parts of the molecules so small that their shapes are not changed over the temperature, pressure and composition range considered. The argument which follows would not be otherwise changed by this more detailed treatment.

^{M} (mixing) and a subscript $_v$ (volume) for the first change, and with a superscript ^{M} for the second change, but will use the subscript $_p$ (pressure) for this change only when it is desirable to emphasize the distinction from the change at constant total volume. The difference between this increment and the corresponding one for an ideal solution will be designated with a superscript ^{E} (excess).

We assume: (1) that *the mutual energy of two molecules is a function only of their relative position and orientations as given by the co-ordinates* $x_1 \ldots x_6$, *and depends not at all on the nature of the other molecules between or around them or on the temperature;* and (2) that *the distribution function for any pair of molecules is also independent of the temperature and the nature of the other molecules present.* Then the multiple integral is also independent of the temperature and the composition of the system, although it does depend upon the volume, and may be considered a function of the molal volume of any component. We shall abbreviate this multiple integral as $a_{jk}V_jV_k$.

The energy may be expressed as

$$E = \Sigma_j N_j E_j^0 + [\Sigma_j N_j \Sigma_k N_k a_{jk} V_j V_k]/V.$$

Applying this equation to the initial and the first final state, we obtain

$$\begin{aligned} E_v^M &= [\Sigma_j N_j \Sigma_k N_k V_j V_k (a_{jk} - a_{jj})]/(\Sigma_k N_k V_k) \\ &= [\Sigma_j z_j \Sigma_k z_k (a_{jk} - a_{jj})](\Sigma_k N_k V_k), \end{aligned}$$

in which $z_j = N_j V_j/(\Sigma_k N_k V_k)$. Moreover, it follows from the second assumption that the entropy change for the first change of state is the same as for the corresponding change with perfect gases, or

$$S_v^E = S_v^M + R\Sigma_j N_j \ln (N_j/\Sigma_k N_k) = 0.$$

Therefore the excess, or non-ideal, change in work content is

$$A_v^E = A_v^M - RT\Sigma_j N_j \ln (N_j/\Sigma_k N_k) = E_v^M.$$

To obtain the change in chemical potentials or the activities it is necessary to determine the change in free energy for the second change of state. We assume: (3) that *the change of volume on mixing at constant pressure is zero.* Then the two changes of state are identical, the change in free energy $F_p^M = A_v^M$, and the change in heat content $H_p^M = E_v^M$. The change in any chemical potential and any activity may be obtained simply by differentiation,

$$\mu_i^E = \mu_i^M - RT \ln (N_i/\Sigma_k N_k) = V_i[\Sigma_j z_j \Sigma_k z_k (2a_{ij} - a_{ii} - a_{jk})].$$

All terms containing z_i vanish in this sum, whose nature may be illustrated by the expression for a three component system:

$$\begin{aligned} \mu_1^E &= V_1[(2a_{12} - a_{11} - a_{22})z_2^2 + (2a_{13} - a_{11} - a_{33})z_3^2 \\ &\qquad + 2(a_{12} + a_{13} - a_{11} - a_{23})z_2 z_3] \\ &= V_1[A_{12}z_2^2 + A_{13}z_3^2 + (A_{12} + A_{13} - A_{23})z_2 z_3], \end{aligned}$$

in which $A_{12} = 2a_{12} - a_{11} - a_{22}$, etc. The corresponding expression for the energy change is

$$E_v^M = (A_{12}z_1z_2 + A_{13}z_1z_3 + A_{23}z_2z_3)(N_1V_1 + N_2V_2 + N_3V_3).$$

For a component $a_{jj}V_j$ is the change in energy per mole in going from the perfect gas state to the liquid at the same temperature, and may usually be taken as the energy change on condensation of a mole of the saturated vapour. It should be noted that it is $a_{jj}V_j$, and not a_{jj} which should be independent of the temperature. To determine the properties of a mixture from those of its components, it is necessary to assume further (4) that $a_{jk} = (a_{jj}a_{kk})^{1/2}$.

The first assumption is apparently well justified for ordinary liquids, and needs no further discussion. The second can be no more than approximate. The deviations which arise from the different sizes and shapes of molecules of different species have been discussed by Hildebrand and Wood,[5] and the effect of differences in the energy of attraction on the distribution has been discussed by Guggenheim,[8] by Scatchard and Hamer,[9] and by Hildebrand.[7] The fourth assumption, which must be an even cruder approximation, is also discussed by Hildebrand and Wood,[5] and by Hildebrand.[7]

The third assumption is also only approximately true, and we shall now calculate the change in volume. It is necessary to assume that the effect of this volume change on $F_v^E - E_v^M$ is negligible, an assumption which will be justified later. We also make use of the relation that $(dE/dv)_T$ is approximately equal to $-(E - E^0)/V_0$ for non-polar and slightly polar liquids.[7] In general, we let p be the pressure corresponding to the volume of the mixture v, and let β and β_0 be the coefficients of compressibility of the mixture and of the isolated components, both assumed to be independent of the pressure. Then

$$p - P_0 = -\int_{V_0+V^M}^{v} \mathrm{d}v/\beta v = \frac{1}{\beta}\ln\frac{V_0 + V^M}{v}.$$

$$P - P_0 = \frac{1}{\beta}\ln\frac{V_0 + V^M}{V_0} - \frac{1}{\beta}\ln\left(1 + \frac{V^M}{V_0}\right).$$

$$\mathrm{d}P/\mathrm{d}P_0 = 1 + \frac{1}{\beta}[\mathrm{d}\ln(V_0 + V^M)]/dP_0 - \frac{1}{\beta}[\mathrm{d}\ln V_0]/\mathrm{d}P_0 = \beta_0/\beta$$

We let $E_{\mathrm{I}} = E - E^0$ for the initial state and $E_{\mathrm{II}} = E - E^0$ for the first final state. Then, at constant temperature,

$$\begin{aligned}\mathrm{d}E_{\mathrm{I}}/\mathrm{d}P_0 &= -\beta_0 V_0(\mathrm{d}E_{\mathrm{I}}/\mathrm{d}V_0) = \beta_0 E_{\mathrm{I}}.\\ \mathrm{d}E_{\mathrm{II}}/\mathrm{d}P_0 &= (\mathrm{d}E_{\mathrm{II}}/\mathrm{d}P)(\mathrm{d}P/\mathrm{d}P_0) = \beta E_{\mathrm{II}}\beta_0/\beta = \beta_0 E_{\mathrm{II}},\end{aligned}$$

and

$$\begin{aligned}V^M &= \mathrm{d}F_v^E/\mathrm{d}P_0 - \mathrm{d}E_v^M/\mathrm{d}P_0 = \mathrm{d}E_{\mathrm{II}}/\mathrm{d}P_0 - \mathrm{d}E_{\mathrm{I}}/\mathrm{d}P_0\\ &= \beta_0(E_{\mathrm{II}} - E_{\mathrm{I}}) = \beta_0 E_v^M = \beta_0 F_v^E.\end{aligned}$$

We may also obtain the coefficient of compressibility of the mixture,

$$\begin{aligned}\beta(V_0+V^M) = -\mathrm{d}(V_0+V^M)/\mathrm{d}P_0 &= -\mathrm{d}V_0/\mathrm{d}P_0 - \beta_0\mathrm{d}E^M/\mathrm{d}P_0 = \beta_0(V_0 - V^M).\\ \beta &= \beta_0(1 - V^M/V_0)/(1 + V^M/V_0).\\ (\beta - \beta_0)/\beta_0 &= -(2V^M/V_0)/(1 + V^M/V_0).\end{aligned}$$

The effect on the change in free energy and heat content of the volume change on mixing at constant pressure may be calculated by purely thermodynamic means. Unless there is a very radical change in methods, any future theory of liquid mixtures, either polar or non-polar, will yield E_v^M and A_v^M, and any experimental measurements will correspond to F_v^M or H_v^M, so these calculations will presumably be needed for any theory.

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[8] E. A. Guggenheim, *Proc. Roy. Soc., A*, 1935, 148, 304.

[9] G. Scatchard and W. J. Hamer, *J. Am. Chem. Soc.*, 1935, 57, 1805.

$$F_v^M - A_v^M = (P - P_0)V_0 = \frac{V_0}{\beta}\ln(1 + V^M/V_0).$$

$$F_p^M - F_v^M = \int_{V_0}^{V_0+V^M} v\,\mathrm{d}p = \int_{V_0}^{V_0+V^M} -\,\mathrm{d}v/\beta = -\,V^M/\beta.$$

$$\begin{aligned} F_p^E - A_v^E = F_p^M - A_v^M &= (V_0/\beta)[\ln(1 + V^M/V_0) - V^M/V_0] \\ &= -\,(V_0/2\beta)(V^M/V_0)^2 + \ldots \end{aligned}$$

As we shall see later, (V^M/V_0) is so small that the higher terms in the expansion may be neglected. Carrying out the same process for the entropy, we obtain

$$\begin{aligned} S_p^E - S_v^E = S_p^M - S_v^M &= \int_{V_0}^{V_0+V^M} (\mathrm{d}p/\mathrm{d}T)_v\mathrm{d}v \\ &= \int_{V_0}^{V_0+V^M} \left[(\mathrm{d}P_0/\mathrm{d}T)_v + \frac{\mathrm{d}(1/\beta)}{\mathrm{d}T}\ln\frac{V_0 + V^M}{v}\right]\mathrm{d}v \\ &= V^M(\mathrm{d}P_0/\mathrm{d}T)_v + \frac{V_0\mathrm{d}\ln\beta}{\beta T\mathrm{d}\ln T}\left[\ln\left(1 + \frac{V^M}{V_0}\right) - \frac{V^M}{V_0}\right] \\ &= V^M\alpha_0/\beta_0 - \frac{V_0\mathrm{d}\ln\beta}{2T\mathrm{d}\ln T}\left[\left(\frac{V^M}{V_0}\right)^2 + \ldots\right], \end{aligned}$$

in which the expansion is the same as above, and α_0 is the coefficient of thermal expansion of the isolated components. Combining the two we obtain

$$H_p^M - E_v^M = V^M T\alpha_0/\beta_0 + \frac{V_0}{\beta}\left(1 + \frac{\mathrm{d}\ln\beta}{\mathrm{d}\ln T}\right)[\ln(1 + V^M/V_0) - V^M/V_0].$$

For our purposes the expanded form is sufficiently accurate, and the difference between β and β_0 may be ignored. For a binary mixture to which assumptions (1) and (2) apply

$$\begin{aligned} V^M/V_0 &= \beta_0 A_{12}z_1z_2, \\ F_p^E/V_0 &= A_{12}z_1z_2(1 - \beta_0 A_{12}z_1z_2/2). \end{aligned}$$

Although F_p^E/V_0 does not have the form kz_1z_2, the correction term is so small that deviations from this cause would probably be immeasurably small. Substituting $\beta_0F_p^E$ for V^M in the expression for the entropy yields

$$S_p^E - S_v^E = \alpha_0F_p^E - \frac{\beta_0(F_p^E)^2\,\mathrm{d}\ln\beta}{2V_0T\mathrm{d}\ln T}.$$

If assumption (2) were exact, this would also be $S_p^E = -\,(\mathrm{d}F_p^E/\mathrm{d}T)_p$. The second term may be neglected relative to the first, and we must conclude that our first assumptions lead not to regular solutions in the sense of Hildebrand, for which F^E is independent of the temperature, but rather to solutions for which V_0F^E is independent of the temperature. Since α_0 is of the order of magnitude of 10^{-3}, the deviations from regularity due to this effect should not be large, but it should lead to an appreciable difference between H_p^M and F_p^E.

The experimental material with which to test these results is rather limited. Sameshima[10] has measured the vapour pressures and compositions of benzene-carbon bisulphide at 25°, and Hirobe[11] has measured the heat content and volume changes at the same temperature. Zawidski[12] has measured the vapour pressures and compositions, and Hubbard[13] the volume change for benzene-carbon tetrachloride and for ethyl acetate-ethyl iodide at 50° and for methylal-carbon bisulphide, for acetone-carbon bisulphide and for acetone-chloroform at 35·17° Of these Hirobe has measured the heat content change at 25° for benzene-carbon tetrachloride. Except for the volume change for acetone-chloroform, the curves all have approximately the form of our equations. It is therefore sufficient to compare the interpolated values at equal volume fractions of the two components. Such a comparison is given in Table I.

TABLE I.

System.	V^M/V_0.	F^E/V_0.	H^M/V_0.	$-(E_I/V_0)(V^M/V_0)$.	$-(V^M/V_0)^2/2\times 10$
$C_6H_6-CS_2$ . .	0·0076	36	70	30	−0·29
$C_6H_6—CCl_4$ . .	0·0006	12	12	2	−0·002
$C_2H_5O_2C_2H_3—C_2H_5I$	0·0092	33	-	32	− 0·42
$CH_2(OCH_3)_2—CS_2$.	0·0131	87	-	47	−0·86
$(CH_3)_2CO—CS_2$.	0·0153	156	--	64	−1·17
$(CH_3)_2CO—CHCl_3$.	−0·0019	−76	−244	−7	−0·018

Those of the coefficients of compressibility which have been measured are 10^{-4} reciprocal atmospheres within a few per cent., so the comparison is made on the assumption that all have this value. The second column is V^M/V_0, the third is F^E/V_0, the fourth is H^M/V_0, all measured. The fifth column is $T(S_p^E - S_v^E)/V_0$ calculated from $-(E_I/V_0)(V^M/V_0)$, and the sixth is $(F_p^E - A_v^E)/V_0$ calculated from $-(V^M/V_0)^2/2 \times 10^{-4}$. The last four columns are expressed in atmospheres.

We exclude the last system from consideration for the moment. The second column never exceeds 2 per cent. The ratio of V^M to its calculated value, $10^{-4}F^E$, varies from 0·5 for benzene-carbon tetrachloride to 2·8 for ethyl acetate-ethyl iodide. The theory appears to give results somewhat better than the order of magnitude, and to be no better for the non-polar mixtures than for slightly polar ones. The ratio of $-(F_p^E - A_v^E)$ to F_p^E varies from 0·02 per cent. for benzene-carbon tetrachloride to 1·3 per cent. for ethyl acetate-ethyl iodide and is usually a little less than 1 per cent. We are therefore fully justified in neglecting this correction term in calculating either F^E or V^M. Since d ln β/d ln T is usually about unity, the corresponding term in — $(H_p^M - E_v^M)$ is usually about twice as large as for — $(F_p^E - A_v^E)$, but is still not more than about 1 per cent. of H_p^M. The term which arises from the entropy change with changing volume is, however, much larger. Its ratio to F_p^E varies from 17 per cent. for benzene-carbon tetrachloride to 97 per cent. for ethyl acetate-ethyl iodide. The fourth column minus the sum of the third and the fifth should give the absolute temperature times the excess entropy of mixing at constant volume. This is positive for the first system and negative for the second, but it is not certain that either is greater than the experimental errors.

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[10] Sameshima, *J. Fac. Sci. Tokyo*, 1925, 1, 63.
[11] Hirobe, *ibid.*, 1925, 1, 155.
[12] Zawidski, *Z. physik. Chem.*, 1900, 35, 129.
[13] Hubbard, *ibid.*, 1910, 74, 217.

For acetone-chloroform, V^M/V_0 in relation to z is very unsymmetrical, and V^M is probably positive for solutions rich in acetone. However, its value is always so small that the effect on the free energy and even on the heat content is almost negligible. The irregularities of this system are probably connected with the facts that two molecules of the same kind cannot approach each other closely with their dipoles parallel and colinear, but a chloroform and an acetone molecule can approach each other closely in this position, and that the two molecules have very different shapes.

Hirobe has also measured the volume and heat content changes on mixing at constant pressure for a large number of other systems. Our theory would lead us to expect that V^M/H^M should be somewhat less than 10^{-4} if the former is expressed in cubic centimetres and the latter in cubic centimetre-atmospheres. Of the systems studied, not containing a hydroxyl group, the ratio varies with the composition for carbon bisulphide-ether, benzene-ethyl acetate, and ether-acetone. The systems which give approximately constant ratios, with the ratios times 10^4 in parentheses, are: benzene-pinene (0·8), carbon bisulphide-pinene (1·2), carbon bisulphide-carbon tetrachloride (1·1), carbon bisulphide-ethylene bromide (0·5), carbon bisulphide-chloroform (0·9), carbon bisulphide-paraldehyde (1·1), carbon bisulphide-ethyl acetate (1·0), carbon tetrachloride-ethylene bromide (0·1), carbon tetrachloride-chloroform (0·7), benzene-chloroform (— 0·4), chloroform-paraldehyde (0·2), chloroform-ethyl acetate (0·0), ether-ethyl acetate (— 0·8). The agreement of the non-polar mixtures is again fair, but a polar component may introduce considerable irregularity. Negative ratios, shown by only two of the systems listed above, are common with mixtures containing an alcohol.

The comparison of the entropy change at constant pressure with the difference between the entropy at constant pressure and at constant volume can also be made from other measurements. The only equilibrium measurements with organic liquids which cover a large enough temperature range to determine the temperature coefficients are measurements of the solubility of solids. These are complicated by the fact that the heat of fusion must be known accurately as a function of the temperature, and because the composition is changing with the temperature. For iodine dissolved in titanium tetrachloride and in silicon tetrachloride $V\mu^E$ is independent of the temperature, but for the solution in carbon bisulphide μ^E itself is more nearly constant, and in ethylene dibromide both increase.[14] The difference is in any case small, for the coefficient of thermal expansion of organic liquids is about 10^{-3}. The best test may probably be obtained from the measurements of the electromotive force of liquid amalgam cells, although α for liquid metals is only about $0{\cdot}15 \times 10^{-3}$. For cadmium in tin and in lead, and for zinc in cadmium,[15] this accounts for about half of the temperature coefficient of μ^E, but for thallium in tin,[16] it accounts for only one-tenth of the temperature change. It appears that for all these alloys the entropy of mixing at constant volume is positive, and that for the last mixture it has a quite considerable magnitude.

We may conclude that the volume change on mixing at constant pressure may be calculated approximately from the change in free energy or heat content, or may be calculated from the energies of evaporation of the components about as accurately as these two quantities. The effect of this volume change on the entropy of mixing is considerable, and it has a large effect on the calculation of the heat content change on mixing at constant pressure from the energy change at constant volume, but has very little effect on the calculation of the free energy change at constant pressure.

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[14] G. R. Negishi, L. H. Donnally and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1933, 55, 4793.

[15] N. W. Taylor, *ibid.*, 1923, 45, 2865.

[16] J. H. Hildebrand and J. N. Sharma, *ibid.*, 1929, 51, 462.

THE LAWS OF SOLUBILITY.

By M. G. Evans.

Received 24th August, 1936.

The mole fraction x of a solute in a solution can, in a large number of cases, be expressed over a fairly wide temperature range by the equation (1)

$$\log_{10} x = \log_{10}e \cdot \frac{H}{RT} - b. \quad . \quad . \quad . \quad . \quad (1)$$

In this expression H is the heat of solution of the solute and b can be identified with $\log_{10}e\,\frac{S}{R}$, where S is the entropy change accompanying solution.

If the solvents and solutes which obey equation (1) were to form ideal solutions H would be the latent heat of fusion of the solute λ_f and $b = \log_{10}e \cdot \frac{\lambda_f}{RT_f}$ where T_f is the absolute temperature of fusion of the solute

$$\log_{10} x = \log_{10}e \cdot \frac{\lambda_f}{RT} - \log_{10}e \cdot \frac{\lambda_f}{RT_f}.$$

TABLE I.

Solute.	p 10^4.	C.	λ_f Cals.	T_f (°A)	b $\log_{10}e\,\frac{\lambda_f}{RT_f}$.	$b_{calc.}$
Benzoic acid . .	5·43	0·057	4·14	394·4	2·28	2·30
Naphthalene . .	6·16	0·016	4·56	353·1	2·80	2·82
Phenanthrene . .	5·84	0·016	4·32	372·0	2·52	2·54
o-Dinitrobenzene .	5·34	0·102	5·46	389·5	3·04	3·02
Benzene . . .	7·84	0·000	2·37	278·5	1·85	1·86
Carbazole . .	4·57	—0·221	7·03	509·1	2·99	3·00
Nitrobenzene . .	7·79	0·022	2·77	278·3	2·17	2·18
o-Nitrophenol . .	6·96	—0·042	3·73	317·0	2·55	2·55
p-Dinitrobenzene .	4·13	0·472	6·71	446·5	3·27	3·25
m-Dinitrobenzene .	5·94	0·030	4·15	362·0	2·48	2·48
α-Chloracetic acid .	6·55	—0·017	2·80	334·7	1·82	1·83
Phenol . . .	6·92	0·008	2·73	313·6	1·89	1·90
Benzoyl chloride .	8·06	—0·023	—	272·8	—	—
Ethylenedibromide .	6·05	0·466	—	282·7	—	—
Fluorene . . .	5·63	0·006	—	387·5	—	—
Acenaphthene . .	5·87	0·040	—	368·0	—	—

For the case of the same solute in a series of solvents all of which form ideal solutions the heat of solution λ_f and the entropy of solution λ_f/T_f would be identical for all solvents. There are a large number of cases in which ideal solutions are not formed, that is, in which the heat of solution is not identical with the heat of fusion, but in which the heat of solution and the entropy term b are connected by the simple relationship

$$b = \rho H + c. \quad . \quad . \quad . \quad . \quad (2)$$

We have discussed this relationship in connection with collision numbers in solution in a previous paper,[1] and there the general scope of the equation is set out in Fig. 2 and the actual data in Table I. We summarise the values of ρ and c in Table I. of the present communication.

TABLE II.

Solute.	ρT_f.	(ρT_f − 0·2172).
Benzoic acid	0·2140	− 0·0032
Naphthalene	0·2179	+ 0·0007
Phenanthrene	0·2172	0·0000
o-Dinitrobenzene	0·2077	− 0·0095
Benzene	0·2181	+ 0·0009
Acenaphthene	0·2160	− 0·0012
Carbazole	0·2323	+ 0·0151
Nitrobenzene	0·2162	− 0·0010
o-Nitrophenol	0·2203	+ 0·0031
p-Dinitrobenzene	0·1840	− 0·0332
m-Dinitrobenzene	0·2150	− 0·0022
α Chloroacetic acid	0·2190	+ 0·0018
Phenol	0·2182	+ 0·0010
Benzoyl chloride	0·2200	+ 0·0028
Ethylenedibromide	0·1710	− 0·0462
Fluorene	0·2180	+ 0·0008

If the solvent formed were ideal the value of b would be given by

$$\log_{10}e \cdot \frac{\lambda_f}{RT_f}$$

and of H given by λ_f. It is seen from the last two columns of Table I., where the values of b calculated from the latent heat and the temperature of fusion are compared with those calculated from the constants of equation (2), that ideal solutions also obey that equation. From Fig. 2 of our previous paper it was apparent that the spread of the straight lines for various solutes followed the fusion temperature of the solid solutes. In Table II. we show the value of ρT_f for the various solutes employed. If the solutes formed ideal solutions ρT_f would be equal to

$$\frac{\log_{10} e}{R} = 0{\cdot}2172.$$

It appears, therefore, that if we neglect the constant terms, which are in most cases small, we can express equation (2) as approximately

$$\frac{S}{R} \approx \frac{H}{RT_f}.$$

That is, not only in the cases in which ideal solutions are formed but in most of the cases obeying equation (2) the entropy of solution is given by the heat of solution divided by the temperature of fusion.

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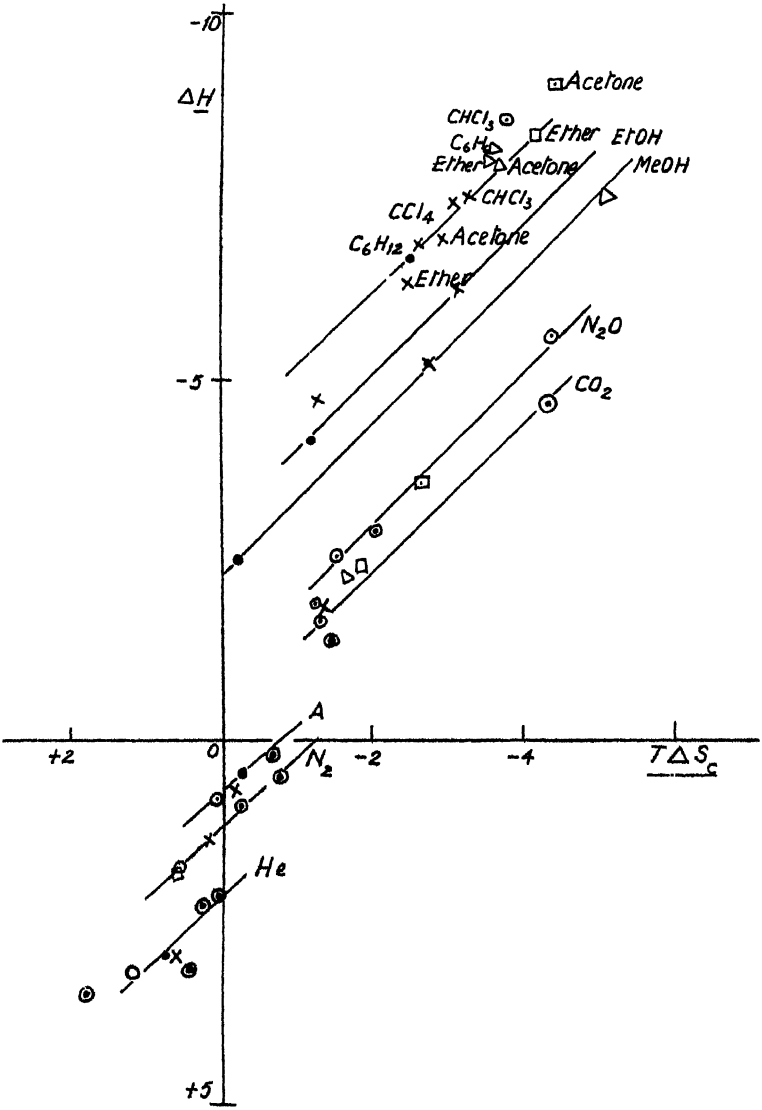
[1] *Trans. Faraday Soc.*, 1936, **32**, 1333.

*GENERAL DISCUSSION.**

Professor J. H. Hildebrand (*Berkeley, Cal.*), said: The subject dealt with by Professor Scatchard has been slurred in previous studies, and it is very gratifying to have a careful analysis of it.

Dr. J. A. V. Butler (*Edinburgh*) said, with regard to Dr. Evan's paper I would like to make some remarks about the relation between the heat and entropy of solution, because we have been approaching similar ideas



Heats and Entropies of Solution. The solvents are as follows :—
C_6H_6, × ; C_6H_{12}, ● ; CCl_4, △ ; $CHCl_3$, ⊡ ; $(CH_3)_2CO$, ⊙ ; Other Solvents, ⊙.

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* On the two preceding papers.

in another connection. The figure shows the results at present available. For the systems shown in the upper part of the figure, the free energy of solution has been determined by Mr. W. S. Reid by measurements of the vapour pressure in dilute solution, while the heats of solution are calorimetric values recorded in the literature. It will be seen that for ethyl and methyl alcohol there is a linear relation between ΔH and ΔS and, though measurements in few solvents are available for other solutes, there are indications of a similar relation. In the case of the gases shown in the lower part of the diagram, both ΔH and ΔS are calculated from the temperature coefficient of the solubility and are thus not independent. In fact, even if the temperature coefficients employed were incorrect, the figures calculated would still show this relation. This is because the solubilities of the gases in the various solvents differ comparatively little and the free energy of solution apparently varies much less than the heat of solution. Since $\Delta F = \Delta H - T\Delta S$, it is evident that if ΔF is approximately constant, ΔH and ΔS are necessarily proportional to each other. The fact that the free energies of solution differ little in a series of solvents is itself a proof of the linearity between ΔH and ΔS.

The heats and entropies of solution of solids given by Polanyi and Evans [2] are also both derived from the solubility and the same circumstances may apply. While these data are no doubt of much greater accuracy than the solubilities of gases, and there is no reason to question that they demonstrate linear relations between the entropies and heats of solution of a given solute in various solvents, it seems to me that the further relation concerning the values of the proportionality constants, which is suggested by Evans in this paper is less firmly based. For the heats and entropies of solution given are identified with the constants A and B in the empirical solubility equation $R \log N = A/T + B$. This identification is not exact, except when the solutions are quite dilute, and the accurate value of ΔH is $\Delta H = A - d(\log f)/d(1/RT)$, where f is the activity coefficient in the saturated solution, which may vary both with temperature and composition. If it were possible to take this factor into account somewhat different slopes of the $\Delta S - \Delta H$ relation for a given solute in a series of solvents might be obtained.

Turning now to the theoretical basis of such a relation, Evans and Polanyi have introduced an environmental factor χ which is supposed to be capable of variation by infinitesimal amounts. On the assumptions that at absolute zero $dS/d\chi = 0$ and $dF/d\chi = \beta^\circ$, where S and F are the entropy and free energy of solution, they show that there is a proportionality between S and H at a finite temperature. An alternative formulation of the thermodynamical quantities is as follows. Let $dH/d\chi = \beta_0$ at $T = 0$, and let C_χ and C_0 be the heat capacities in the states χ and $\chi = 0$; then on the assumption that $dS/d\chi = 0$ at $T = 0$, we obtain :

$$H_\chi^T - H_0^T = \int_0^T (C_\chi - C_0)\,dT + \beta_0\chi;$$

$$S_\chi^T - S_0^T = \int_0^T \left(\frac{C_\chi - C_0}{T}\right)dT$$

$$F_\chi^T - F_0^T = \beta_0\chi + \int_0^T (C_\chi - C_0)\,dT\cdot$$

If $C_\chi - C_0$ is also proportional to χ, *i.e.*, if the change of the heat capacity is proportional to the change of the heat of solution, this obviously leads to a proportionality between the heats and entropies of solution. In general, $T\int_0^T (C_\chi - C_0/T)\,dT$ may be expected to be greater than $\int_0^T (C_\chi - C_0)\,dT$, so that the variation of F with the parameter χ is smaller than that of H, and also smaller, and possibly of the opposite sign to the variation of H at absolute zero. This may explain why the variation of the free energy of a solute in a series of solvents is so much smaller than the variation of H.

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[2] *Trans. Faraday Soc.*, 1936, 32, 1333.

Professor J. H. Hildebrand (*Berkeley, Cal.*) said: The families of solubility curves which I have published for such substances as iodine and sulphur will be found, I believe, to contain the relation between heat and entropy given by Evans, or something akin to it. They also suggest the regions and the systems where the relation may prove to be rather more complicated.

Professor M. Polanyi (*Manchester*) said: I do not see that the linear relationships between entropy and heat which Mr. Evans and I have pointed out depend on the assumption that $\frac{\partial S}{\partial \chi} = 0$ and $\frac{\partial H}{\partial \chi} = \beta'$ at the absolute zero. The considerations which we have based on the Nernst heat theorem are used only to explain the fact that the changes of TS are opposite in sign to, and smaller than those of, H. Our discussion shows that the change of the heat capacity with χ determines these features. The same principle is demonstrated by the deduction of Dr. Butler

Mr. M. G. Evans (*Manchester*), in reply (*communicated*): As Professor Hildebrand suggests, the linear relationship which we have discussed is contained in the families of curves relating the freezing-point depression and the logarithm of the mole fraction of solute. Clearly, the relationship $S/R = pH + C$ cannot hold over the whole range of $\log N$, since it implies intercepts of the $\log N = 0$ line at different points for different heats of solution of the same solute in a series of solvents, whereas all the curves by definition must meet at $1/T_f$, T_f the temperature of fusion of the solute.

Referring to Dr. Butler's point about the variation of activity coefficient with temperature and composition, the linear relations discussed are for those ranges of temperature and concentration for which, in the case of a particular solvent, the same solubility expression $\log N = \frac{A}{RT} + B$ applies over the whole range, which, in most cases, is a considerable one. If the identification of the heat and entropy terms with A and B is valid at small concentrations, it must also be valid over the whole range where the same A and the same B are applicable.

The expression given by Dr. Butler can be obtained from the relationships given in the paper of Evans and Polanyi:

$$\left(\frac{\partial H}{\partial \chi}\right)_T = \beta' + \int_0^T \left(\frac{\partial \beta}{\partial T}\right)_\chi \mathrm{d}T - \left(\frac{\partial \beta}{\partial T}\right)_\chi$$

$$\left(\frac{\partial S}{\partial \chi}\right)_T = \left(\frac{\partial \beta}{\partial T}\right)_\chi = \int_0^T \frac{\partial (c/T)}{\partial \chi} \mathrm{d}T$$

$$\int_0^T \left(\frac{\partial \beta}{\partial T}\right)_\chi \mathrm{d}T - \left(\frac{\partial \beta}{\partial T}\right)_\chi = -\int_0^T T \frac{\partial^2 \beta}{\partial T^2} \mathrm{d}T = \int_0^T \frac{\partial C}{\partial \chi} \mathrm{d}T,$$

leading to equations identical with the integrated expressions given by Dr. Butler.

THE ACTIVITIES OF SOME ALIPHATIC ALCOHOLS AND HALIDES IN NON-POLAR SOLVENTS.

By J. A. V. Butler and P. Harrower.

Received 3rd September, 1936.

It appears that the chief types of interaction of molecules in solutions have now been recognised. They are (1) that due to the van der Waals' or dispersion forces, the approximate value of which for any two atoms is given by London's expression; (2) the interaction of electric dipoles with other dipoles on the one hand and with polarisable molecules (induced dipoles) on the other; (3) the interaction of electrically charged particles with each other, with dipoles and with polarisable molecules; (4) the interaction of two molecules involving compound formation by the mutual sharing of electrons.

In the absence of effects of type (4), which are rare between non-polar substances, non-polar solutions should be capable of being accounted for by (1). If the average disposition of molecules round a given molecule were accurately known there would be no difficulty in applying London's expression to determine the energy of interaction. Hildebrand and Wood[1] have made use of probability functions for this purpose, and on certain assumptions has obtained for the energy of transfer of a molecule from its pure liquid to a given solution:

$$\phi = V_2\left\{\left(\frac{E_2}{V_2}\right)^{\frac{1}{2}} - \left(\frac{E_1}{V_1}\right)^{\frac{1}{2}}\right\}^2 v_1^2,$$

where V_2 is the molecular volume of the solute considered, V_1 that of the solvent; E_1, E_2 their energies of vaporisation from the pure liquids, and v_1 the volume fraction of the solvent in the solution. On the assumption that the entropy change in the transfer is zero, ϕ is identified with the free energy of the transfer $RT \log f$.

A simpler treatment of these forces which shows up the physical considerations involved is as follows. London's expression for the mutual potential of two like atoms at a distance r_{11} is $\phi_{11} = 3/2 \cdot \epsilon_1^2/2\epsilon_1 \cdot \alpha_1^2/r_{11}^6$ and that of two different atoms at a distance r_{12} is

$$\phi_{12} \geqq 3/2 \cdot \epsilon_1\epsilon_2/(\epsilon_1 + \epsilon_2) \cdot \alpha_1\alpha_2/r_{12}^6,$$

where ϵ_1, ϵ_2 are the excitation potentials and α_1, α_2 the polarisabilities of the atoms. These expressions diminish so rapidly with distance that for practical purposes in liquid systems it is only necessary to consider the interaction of adjacent atoms. The energy of a molecule in a liquid is thus obtained by summing the interactions of its atoms with the adjacent atoms of surrounding molecules. It follows that Langmuir's "principle of independent surface action"[2] is a legitimate and useful method of dealing with interactions of this type. In terms of this theory, it has been shown[3] that the difference between the energy of a molecule B in a dilute vapour and in a very dilute solution in a solvent A is $S_a(\gamma_{aa}/2-\gamma_{ab})$, where S_a is the surface area of the molecule, γ_{aa} the cohesive energy of two unit surfaces of the solvent and γ_{ab} the adhesive energy of unit surface of the solute with the solvent. The first term in this expression is the energy required to produce in the solvent a cavity large enough to hold the dissolved molecule, the second the energy of introducing the solute molecule into the cavity.

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[1] *J. Chem. Physics*, 1933, 1, 817; Hildebrand, *J. Amer. Chem. Soc.*, 1935, 57, 866.

[2] *Coll. Symp. Monographs*, 1925, 3, 48.

These quantities can be expressed in terms of the London potential if certain approximations are made. Writing $\phi_{11} = \theta_{11}^2$, and assuming that the average distance of two unlike adjacent atoms is the geometrical mean of the distances of two like atoms, *i.e.*, $r_{12}^2 = r_{11}r_{22}$, we have approximately $\phi_{12} \geqq \theta_{11}\theta_{22}$. Taking the equality as correct, the energy of interaction between a molecule and its surrounding molecules is then given by $\Sigma\theta_{11}\theta_{22}$, where the summation is made for each atom in the molecule with the adjacent atoms of solvent molecules. Similarly the energy required to make the cavity may be expressed as $\frac{1}{2}\Sigma\theta_{11}^2$, where the summation applies to the atoms at its surface. Thus the energy of introducing a solute molecule is

$$\phi = \frac{1}{2}\sum_{surface}\theta_{11}^2 - \sum\theta_{11}\theta_{22}.$$

For simple solute molecules related in a regular way, *e.g.*, in a homologous series ϕ may be expected to increase by regular increments for the first term is proportional to the size of the cavity and the second is additive for the parts of the solute molecule.

The energy of transfer of a molecule from its pure liquid into a dilute solution in a given solvent is similarly

$$\phi = \frac{1}{2}\sum_{surface}\theta_{11}^2 - \sum\theta_{11}\theta_{22} + \frac{1}{2}\sum_{surface}\theta_{22}^2,$$

where the last summation is the work of removing a molecule from its pure liquid. Now if the area of the molecule is S, a_{11} the number of contacts per unit area between the solute molecule and solvent molecules and $\bar{\theta}_{11}^2$ the average value of θ_{11}^2 for the various contacts, etc., this may be written as

$$\phi = \frac{1}{2}S(a_{11}\bar{\theta}_{11}^2 - 2a_{12}\bar{\theta}_{11}\bar{\theta}_{22} + a_{22}\bar{\theta}_{22}^2),$$

or if a_{11} and a_{12} do not differ greatly:

$$\phi = \frac{1}{2}S(a_{11}^{\frac{1}{2}}\bar{\theta}_{11} - a_{22}^{\frac{1}{2}}\theta_{22})^2.$$

But $a_{11}\bar{\theta}_{11}^2$ is the energy of interaction between two unit surfaces of the solvent, *i.e.*, the cohesive energy of the solvent (P_1), and $a_{22}\bar{\theta}_{22}^2$ is the cohesive energy (P_2) of the pure solute, so that we have

$$\phi = \frac{1}{2}S(P_1^{\frac{1}{2}} - P_2^{\frac{1}{2}})^2.$$

This is very similar to Hildebrand's expression,[4] the P's taking the place of the energy densities (E/V). The latter is more convenient to use, since only easily measurable physical magnitudes appear in it.

The next case is that of dipole molecules in non-polar solvents where the electrostatic energy of the dipoles is superimposed on the dispersion energy. Martin[5] and Bell[6] have given expressions for this as a function of the dielectric constant of the medium. The latter has found that the free energy of transfer of dipole molecules in dilute solution from one solvent to another (including polar solvents) can be approximately accounted for, and the former has attempted to extend the application to concentrated solutions in which the dielectric constant is largely determined by the solute. In such solutions there are two cases to be considered, according to whether dipole associates of two or more molecules are formed. It is well known that acids, phenols, etc., are present as double molecules even at quite small concentrations in solvents of low dielectric constant. It has been shown[7] that the undissociated salt molecules may be formed in a salt solution when the dissociation energy of the salt exceeds the loss of solvation energy of the ions. Similarly it may be expected that dipole association will take place when the energy of interaction of the dipoles with each other in the associate is greater than their individual energies of interaction with the solvent. Thus dipole association will occur when the interaction energy of the two dipoles is large and preferentially in solvents of low dielectric constant. The hydroxyl, carboxyl and similar groups, owing to the distribution of electrons brought about by the presence of the proton, have a particularly large energy of association (ca. 5000 cals.), produced by the interaction of the proton of one molecule with a centre of negative charge in the other (the " hydroxyl bond " of Bernal.[8] In halides and similar molecules having equally great dipole moments, the only interaction of the dipoles sterically possible is the side by side interaction as $\pm\mp$, which generally has a considerably smaller energy. Hence we should expect a greater tendency to associate in the first than the second class of compounds.

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[3] Butler, Thomson and Maclennan, *J. Chem. Soc.*, 1933, 681.

[4] In Hildebrand's derivation the interaction of two molecules is calculated on the assumption that the polarisation of the whole molecule is located at its centre. At short distances of approach this differs considerably from that obtained if each atom or group is supposed to act as a polarisable centre. For a precise calculation the distribution and nature of the outer electrons would have to be taken into account.

In order to obtain further data for testing these conclusions measurements have been made of the activity coefficients of some aliphatic alcohols and some of the corresponding halides in dilute solutions in non-polar solvents. Dilute solutions of the " solvents " in each other were also examined, and provide further material for the discussion of the effect of dispersion forces.

Experimental.

The vapour pressures were determined by bubbling a slow stream of air through the solutions in the apparatus used for aqueous solutions and freezing out the condensate in a CO_2-ether mixture.[9] The condensates were analysed by comparison with suitable calibration solutions in a Hilger-Rayleigh refractometer. The solvents were carefully dried and fractionated before use and had the following corr. b.pts.: benzene 79·9°; carbon tetrachloride 76·5°; cyclohexane 80·6°. Blank experiments were made in which the condensates formed under similar conditions from the pure solvents were compared in the interferometer with the original liquids. The difference was negligible with benzene and carbon tetrachloride, but in the case of cyclohexane the condensate differed from the original solution by 8 drum divisions, which was subtracted from the readings of the various condensate solutions.

[5] *Phil. Mag.*, 1929, 8, 550.

[6] *Trans. Faraday Soc.*, 1931, **27**, 797.

[7] Orr and Butler, *Phil. Mag.*, 1934, 18, 778.

[8] *Proc. Roy. Soc.*, 1935, **151**, 384.

[9] Butler and Shaw, *Ibid.*, *A*, 1930, **129**, 519.

TABLE I.—PARTIAL VAPOUR PRESSURES IN BENZENE AND CARBON TETRACHLORIDE AT 25°.

Solute.	Solvent: Benzene.				Solvent: Carbon Tetrachloride.			
	$N \times 10^2$.	$x \times 10^2$.	p.	p/N.	$N \times 10^2$.	$x \times 10^2$.	p.	p/N.
MeOH .	0·053	1·45	1·39	2620	0·072	1·93	2·25	3130
EtOH .	0·203	2·06	1·97	970	0·186	1·87	2·18	1170
PrOH .	0·094	0·303	0·286	300	0·100	0·335	0·384	380
BuOH .	0·085	0·086	0·080	97	0·115	0·129	0·148	129
PrCl .	0·746	2·67	2·57	340	0·692	2·63	3·06	440
PrBr .	1·072	1·54	1·46	140	1·237	1·80	2·07	167
PrI .	—	—	—	—	0·896	0·35	0·399	41
BuCl .	1·251	1·40	1·33	106	1·231	1·44	1·653	131
BuBr .	1·697	0·90	0·84	49	1·238	0·68	0·781	63
BuI .	—	—	—	—	1·401	0·20	0·227	16
$BuNO_2$.	1·094	1·33	1·26	—	1·730	2·18	0·513	145

It has been shown that in very dilute solutions the partial pressure of the solute can be obtained from the composition of the condensate alone, when the vapour pressure of the pure solvent is known. The following v.ps. at 25° were assumed: benzene 94·4 mm.; carbon tetrachloride 114·5 mm.; cyclohexane 96·2 mm. The alcohols were determined in solutions of ca. 0·1 mols. per cent., while in the other cases the molar fraction of the solute was of the order of 1 per cent. The experimental results are given in Tables I. to III. N is the molar fraction of the solute in the solution, x its molar fraction in the condensate, and p the partial pressure of the solute at 25°. Each result is the mean of at least two concordant experiments. The method of analysis depends on there being an appreciable difference of refractive index between the two components. In certain cases, for which no data are given, the difference was too small for the method to be practicable. The propyl and butyl compounds are all the *normal* derivatives.

TABLE II.—PARTIAL PRESSURES IN CYCLOHEXANE.

Solute.	$N \times 10^2$.	$x \times 10^2$.	p.	p/N.
PrCl .	1·193	5·98	6·05	510
PrI .	2·347	1·40	1·33	57
BuCl .	1·221	1·91	1·85	152
BuI .	2·720	0·70	0·66	24
$BuNO_2$.	1·431	2·82	2·82	190

TABLE III.—PARTIAL PRESSURES OF NON-POLAR SUBSTANCES IN EACH OTHER.

Solute.	Solvent.	$N \times 10^2$.	$x \times 10^2$.	p.	p/N.
C_6H_{12}	C_6H_6	1·474	2·51	2·39	163
CCl_4	C_6H_6	1·246	1·65	1·56	125
C_6H_6	CCl_4	1·638	1·57	1·80	110
C_6H_{12}	CCl_4	1·148	1·16	1·33	115
C_6H_6	C_6H_{12}	1·393	2·35	2·28	164
CCl_4	C_6H_{12}	1·002	1·53	1·48	148

Discussion.

The Activity Coefficients of the Non-polar Substances in each other are given in Table IV. In these solutions the energy of solution should be determined by the dispersive forces alone. Hildebrand has found that his expression (1), which is based on the assumption that the interaction energy of two unlike molecules is the geometrical mean of the interaction of two like molecules, although giving in general the right order usually gives calculated values of the activity coefficients which are smaller than those observed. This is also the case in these examples. The figures are in the order predicted by the theory, but their magnitude is considerably greater, *e.g.*, the calculated coefficients of benzene in CCl_4 and C_6H_{12} from the (E/V) values given in the table are 1·04 and 1·24. It is of interest that the corollary of Hildebrand's theory, *viz.*, that with substances of about the same molecular volume, the activity coefficient of A in dilute solution in B is equal to that of B in dilute solution in A, holds approximately in these solutions.[10]

TABLE IV.—ACTIVITY COEFFICIENTS OF THE NON-POLAR "SOLVENTS" IN EACH OTHER.

Solute.	V.	E.	$(E/V)^{\frac{1}{2}}$.	Activity Coefficient in		
				C_6H_6.	CCl_4.	C_6H_{12}.
C_6H_6	89	7210	9·00	1	1·17	1·73
CCl_4 .	97	7080	8·54	1·09	1	1·29
C_6H_{12} .	109	6600	7·80	1·69	1·20	1

Additivity of the Free Energies of Solution.—The first point which emerges from a consideration of the p/N values of the alcohols and halides is that, notwithstanding the large activity coefficients of the latter (see below) the free energies of solution from the vapour (*viz.*, $RT \log p/N$) are *additive* in each of the three solvents. The following table shows the values of $RT \log p/N$, and it can be seen that in each case there is a decrement of *ca.* 600 cals. for each additional $-CH_2$ group. This additivity is in accordance with the theory given above (p. 172).

TABLE V.—FREE ENERGIES OF SOLUTION OF ALIPHATIC ALCOHOLS AND HALIDES AT 25°.

Radical.	Benzene.			Carbon Tetrachloride.				Cyclohexane.	
	—OH.	—Cl.	—Br.	—OH.	—Cl.	—Br.	—I.	—Cl.	—Br.
Me . .	4660	—	—	4770	—	—	—	—	—
Et . .	4070	—	—	4190	—	—	—	—	—
Pr . .	3390	3400	2910	3530	3610	3030	2250	3690	2400
Bu . .	2710	2760	2310	2880	2900	2450	1650	2970	1890

Activity Coefficients of the Halides and Alcohols.—Table VI. shows these coefficients for the dilute solutions in the three solvents, obtained by dividing p/N, by the vapour pressures p° of the pure liquids. The latter are not obtained from our own experiments, but from the best values given in I.C.T.

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[10] This also follows from Langmuir's principle of independent surface action, *cf.* Butler, Thomson and Maclennan, *J. Chem. Soc.*, 1933, 682, equation (3).

TABLE VI.—Activity Coefficients of Alcohols and Halides in Dilute Solution in Non-Polar Solvents at 25°.

Solute.	p^0.	V.	E.	$(E/V)^{\frac{1}{2}}$.	$(p/p^0N)_{C_6H_6}$.	$(p/p^0N)_{CCl_4}$	$(p/p\ N)_{C_6H_{12}}$.
MeOH	122·2				21·4	25·6	
EtOH	59·0	—	-	-	16·4	19·9	
PrOH	20·1	—	—	—	15·1	19·1	
BuOH	6·78	--	—	—	14·2	18·8	
PrCl	343	88	6330	8·47	1·01	1·29	1·48
PrBr	137	91	7170	8·88	0·99	1·22	
PrI	43·4	97	7870	8·99	--	1·03	1·31
BuCl	104	105	—	—	1·02	1·20	1·46
BuBr	40	107	—	--	1·23	1·57	

The halides themselves are nearly ideal solutes in benzene and the activity coefficients invariably increase in the order $C_6H_6 < CCl_4 < C_6H_{12}$. This would be the case if E/V for the halides were approximately equal to that of benzene. This is the case with propyl iodide, but the E/V values of the other two, as derived from their vapour pressure equations are smaller. It must be remembered that the derivation of E from a single set of vapour pressures may be unreliable. The order of the values of the different halides in each solvent is Cl > Br > I in the propyl series, and Cl < Br in the butyl series. This would be difficult to account for with any values of E/V which fit in with the solvent order. It is thus probable that the dispersion forces by themselves are not adequate to account for these polar solutes and dipole interactions having the same order of magnitude are superimposed. In these circumstances the two effects cannot easily be distinguished.

The most striking feature of the results is the contrast between the activity coefficients of the alcohols and those of the halides. While the latter are not far from ideal solutes, the activity coefficients of the former range from 14 to 25, *i.e.*, the vapour pressures of the pure alcohols are smaller in this proportion than p/N in the dilute solutions. Since it has been shown that the p/N values are not themselves abnormal, the abnormality must arise from the interaction of the alcohol molecules with each other in the pure liquid. The question remains whether it is a simple dipole interaction of the type envisaged by Martin and Bell, or a definite "association" or polymerisation of the alcohol molecules.

Except in so far as they exhibit a sharp contrast between the alcohols and halides, the measurements given here are not decisive. But it is clear that since the dipole moments of the halide molecules are greater than those of the alcohols, and the effect of the hydrocarbon chain is the same, *e.g.*, in PrCl and PrOH, the only way in which a general dipole interaction (without association) could be made to lead to this result, is by giving the hydroxyl dipole a much smaller radius than those in the halides.

But the possibility of the formation of "hydroxyl bonds" between the alcohol molecules gives a reasonable explanation of their peculiarity and there are other facts, *e.g* the change of polarisation of the alcohols with concentration in non-polar solvents, which also indicate the formation of double and triple molecules.

It may be observed that the " entropy of association " of the alcohols (see below) shows that these abnormally large coefficients decrease rapidly with rise of temperature. The comparatively small activity coefficients which Martin has found [11] in dilute solutions of substances which might be expected to form association " complexes " are thus perhaps due to the comparatively high temperature (70°) at which his measurements were made.

Entropy of Solution of the Alcohols in Benzene.—The measurements of Wolf [12] of the limiting values of the heats of solution of the alcohols in benzene, in conjunction with our values of the free energy, make it possible to determine the entropy of solution. If Q is the heat of solution of the liquid alcohol at infinite dilution and λ its heat of vaporisation at the same temperature, the heat of transfer of the alcohol from the solution to the vapour is $\Delta H = \lambda - Q$. The free energy change in the same process is $\Delta F = -RT \log p/N$, so that the entropy of vaporisation from the dilute solution is $\Delta S_B = (\Delta H - \Delta F)/T$. The values employed, which are in kilocals, except ΔS which is in cals./degs., are given in Table VII. The increase of the entropy change as ΔH increases is discussed elsewhere.[13]

TABLE VII.—ENTROPY OF SOLUTION OF ALCOHOLS IN BENZENE AT 25°.

	Q.	λ.	ΔH.	ΔF.	$T\Delta S_B$.	ΔS_B.	ΔS_l.	ΔS_l-ΔS_B.
MeOH	3·5	9·1	5·6	−4·7	10·3	34·1	40·6	6·5
EtOH	3·7	10·3	6·6	−4·1	10·7	35·5	42·8	7·3
PrOH	3·8	11·4	7·6	−3·4	11·0	36·5	44·1	7·0
BuOH	3·9	12·6	8·7	−2·7	11·8	38·2	46·2	8·0

The table also gives the entropies of vaporisation ΔS_l, referred to the same standard conditions, of the pure liquid alcohols at 25°. The difference $\Delta S_l - \Delta S_B$ is the change of entropy in the transfer of alcohol from the dilute benzene solution to the pure alcohol and is thus a measure of the entropy change in the association (it is not necessarily independent of the solvent). This is of the same order as the excess of the entropy of vaporisation of the alcohols over that of " normal " liquids (average 36).

Distribution Coefficients between Water and Benzene or Carbon Tetrachloride.

These coefficients cannot easily be determined directly since the analysis of alcohols in organic solvents containing traces of water is difficult and the presence of alcohol affects the mutual solubility of water and the organic liquid. They are obtained from our measurements as the ratio of the (p/N) values in dilute solutions in water and the given solvent. From the distribution coefficients the difference of standard free energy in the two solvents can be determined. Conversely it is of interest here to see the relations between the distribution coefficients which arise from the free energy changes in the separate phases discussed here and in the paper on aqueous solutions.[14] The values are given in Table VIII.

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[11] *J. Chem. Soc.*, 1932, 2658 ; 1933, 1413.

[12] *Z. physik Chem.*, *B*, 1935, **28**, 1.

[13] Butler, *this vol.*, p. 235 ; *cf.* also Discussion, p. 168.

TABLE VIII.—Distribution Coefficients of Alcohols.

	$(p/N)_{H_2O}$.	$(p/N)_{C_6H_6}$.	$(p/N)_{CCl_4}$.	$N_{C_6H_6}/N_{H_2O}$.	N_{CCl_4}/N_{H_2O}.
MeOH .	184	2620	3130	0·070	0·059
EtOH .	218	970	1170	0·22	0·18
PrOH .	291	300	380	0·96	0·75
BuOH .	360	97	130	3·49	2·62

It can be seen that these effects give rise to distribution ratios between the non-polar solvents and water which decrease about four times for each additional — CH_2 group. The distribution ratios of the fatty acids between benzene and water, though complicated by association at quite low concentrations, appear to follow a similar relation, indicating that the free energies in the separate phases vary similarly to the alcohols.

Summary.

1. Measurements have been made of the partial pressures of the four lower alcohols and a number of propyl and butyl halides in dilute solutions in benzene, carbon tetrachloride and (in some cases) cyclohexane, and of the three non-polar "solvents" in each other.
2. The activity coefficients of the non-polar substances in each other are in qualitative agreement with Hildebrand's theory, but quantitatively considerably greater.
3. The halides are nearly ideal solutes in benzene and their activity coefficients in the three solvents are in the order $C_6H_6 < CCl_4 < C_6H_{12}$, which may be in accordance with Hildebrand's theory, but their order among themselves indicates the existence of additional factors probably due to their polarity.
4. The activity coefficients of the four lower alcohols in benzene and carbon tetrachloride have much larger values (14 to 25) than the corresponding halides, which it is suggested are due to association through the formation of "hydroxyl" bonds.
5. Combining Wolf's heats of solution with our data, the entropies of solution of the alcohols in solution have been obtained.
6. The distribution coefficients of the alcohols between water and carbon tetrachloride and benzene have been calculated.

We thank the Earl of Moray Fund for a grant for materials, and Messrs. Imperial Chemical Industries for grants which provided part of the apparatus.

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[14] *This vol.*, p. 229.

ON ASSOCIATION, HEAT OF MIXING AND MISCIBILITY GAPS.

By K. L. Wolf (*Würzburg*).

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Molecular Mixtures and Molecular Solutions.

What we call liquids, according to present views, are comparatively close aggregations of molecules, of the same or different kinds, such that no molecule is fixed to a definite point inside the elastic and isotropic fluid : " mixtures of molecules " (*molekulare Gemenge*). The conception of a molecule as a " saturated " group of several linked atoms, with no external field of force and able to move as a unit, whose internal structure is not primarily relevant, has proved its value in the kinetic theory of gases and in structural chemistry. Applying it to liquids (and not taking account of the question of stability) each liquid would appear to be an aggregation of molecules of the same or different kinds,[1] close packed like peas or beans in a sack. Such a " mixture of molecules," in which there are no forces between the single molecules, we call a " molecular mixture " (*molekulare Mischung*). The appearance and behaviour of such "molecularly mixed" liquids as may occur when two liquids are poured together (unlimited miscibility should here as with gases in principle always be possible) is finally determined by the shape of the particles of the molecular mixture.

In reality, such force-free " molecular " mixtures do not occur any more than the completely saturated molecule, or the completely saturated valence. Whenever the intermolecular forces (residual valency) become unimportant for the phenomena in question, *i.e.*, when only the shape arising from the molecules and not their forces influences the phenomena, liquids and liquid mixtures will be treated as " molecular mixtures " (*Mischungen*).

In contrast we have " molecular solutions " (*molekulare Lösungen*), in which the phenomena are mainly determined by the forces[2] between all the molecular parts of the whole, and here, on the other hand, as is frequently carried to excess in kinetic gas theory, the shape of the molecules can sometimes be quite unimportant. Only when these valence or molecular forces are small and of short-range can certain properties of solutions (and, from our point of view, all liquids, are molecular solutions) be explained on the force-free model, and only when the forces are strong and of long-range are the energy relations alone, without reference to the shape of the molecules, sufficient.[3] We must emphasise that what a "molecular mixture or solution" *is* cannot be defined, but only *when* a "mixture of molecules" (*molekulares Gemenge*) behaves as a "molecular mixture" (*Mischung*), *i.e.*, as a sum of chemical individuals, and when as a "solution" (*Lösung*), *i.e.*, as a binding of all the molecules and molecular parts into a whole. The same "mixture of molecules" can behave both as a "molecular solution" and, perhaps at higher temperatures, as a "mixture." The particular nature of the forces causing the "solution" is unessential for this fundamental (morphological) description; it is sufficient that they exist at all. When we come to the examination of actual substances, we shall, however, need a further *graduation of "mixtures" and "solutions."*

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[1] Chemically uniform liquids are therefore to be regarded as " molecular mixtures " or (see below) " supermolecular mixtures " of uniform molecules, while non-uniform liquids (mixtures and solutions in the wider sense, emulsions, etc.) are " mixtures " or " solutions " of different molecules. Crystallisation (formation of two phases) should also be discussed here as well as miscibility gaps of liquids.

[2] *I.e.*, residual valency forces of all kinds, which present themselves nowadays chiefly as the dispersion, induction and electrostatic forces of different orders.

[3] Neglect of both shape and force leads to the most primitive model of matter, *viz.*, the ideal gas ; neglect of shape makes itself felt in the failure of kinetic theories of osmotic pressure, as Fredenhagen has recently shown (*Z. ges. Nat.*, 1935, **1**, 278 ; *Liebig's Ann.*, 1936, **30**, 523).

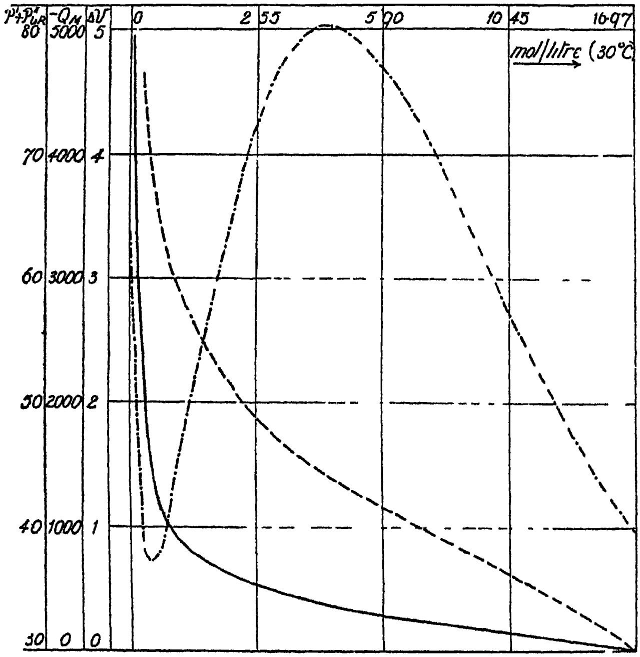

FIG. 1.—Orientation polarisation, heat of mixing and volume of ethanol in cyclohexane.

— · — · — Mol. polarisation, P′ (30° C.).
———— Heat of mixing, Q_M (20° C.).
— — — — $\Delta V \equiv V^{(\mathrm{exp.})}_{M_{12}} - V^{(\mathrm{calc.})}_{M_{12}}$ (30° C.).

That our assumption, which regards, *e.g.*, acetone or ethanol as "solutions" of acetone molecules in acetone or alcohol molecules in alcohol, is reasonable, follows from the comparison of the absorption bands of acetone in pure liquid acetone with those in the vapour or in solutions,[3a] and their alteration with temperature and pressure. In addition to the question of the rise of the boiling-point (so far only investigated with any success for dilute solutions) there is that of the boiling-points of pure liquids, *e.g.*, why do the boiling-points of acetone and *iso*-propyl alcohol differ so markedly, and why are tertiary butyl alcohol and cyclohexane anomalous[4] in their boiling and freezing-points compared

[3a] K. L. Wolf, *Z. physik. Chem.*, *B*, 1928, **2**, 39.
[4] For an attempt at an understanding see H. Pahlke, *Diss.*, Kiel, 1935-36.

with their homologues. How the magnitude of the surface tension and its connection with the heat of vaporisation can be understood from the same point of view may be seen from Trieschmann's investigations [5] on alcoholic solutions.

Our problem also embraces all phenomena of separation (*Entmischung*) up to macroscopic miscibility gaps, the simplest (temperature and concentration dependent) colloids and the precipitation of solids. It begins however with the intrinsically finer distribution (*besserer molekularer Durchmischung*), which occurs in molecular *association*. In Scheibe's recognition [6] that acetone in an equimolecular mixture of alcohol and water is not equally distributed, but associated preferentially with water, and Meerwein's [7] observation that alcohols associate with acetone the more the shorter their hydrocarbon chain, we see from the standpoint of "molecular mixtures" cases of the finest separation. The bimolecular form of acetic acid and alcohols in benzene or hexane, even at the smallest concentrations, we also regard as the first stage of separation. What appear to us macroscopically as liquids are then "mixtures of supermolecules" (*über-molekulare Gemenge*), and we will again distinguish between the "supermolecular mixtures" and "supermolecular solutions," according to whether the liquid behaves as a "mixture" or "solution" of the stoichiometrically complex molecules with the molecules of the hydrocarbon.[8] As the next stage we take "super-molecular mixtures" of molecular parts "dissolved" in each other, e.g. mixtures of two miscible dipolar liquids. That an unbroken line extends from the simplest types of molecular mixtures and solutions, through the simpler grades of "supermolecular mixtures," embracing the phenomenon of association to double molecules, to colloidal mixtures and solutions, is shown by the beautiful investigations on "miscibility gaps" by Vollmer and Moos,[9] who proved that "associ-

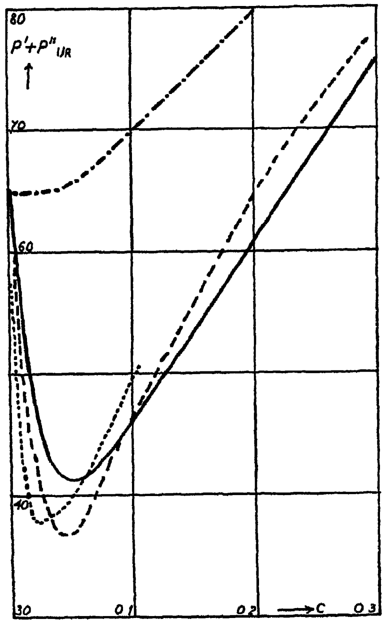

FIG. 2.—Molar orientation polarisations.

6° { ———— Ethanol-hexane.
— — — — Ethanol-cyclohexane.
. . . . . . Methanol-cyclohexane.
30° —·—·— Ethanol-benzene at 30° C.

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[5] H. G. Trieschmann, *Z. physik. Chem.*, *B*, 1935, **29**, 328.

[6] G. Scheibe, *Ber.*, 1925, **58**, 588; *Hand- u. Jahrbuch der chem. Physik*, vol. 9, IV., Leipzig, 1936; also F. O. Rice, *J. Amer. Chem. Soc.*, 1920, **47**, 727.

[7] H. Meerwein and H. Burnleit, *Ber.*, 1928, **61**, 1840; also K. L. Wolf, *Z. physik. Chem.*, *B*, 1928, **2**, 39.

[8] An example of a "supermolecular mixture" is given by much ethanol with little cyclohexane (see Figs. 7 and 8), and of a "supermolecular solution" by much ethanol with little benzene (see Figs. 5 and 5*a*).

[9] M. Vollmer, *Z. physik. Chem.*, 1927, **125**, 151; J. Moos, *Diss.*, Berlin, 1933; see also R. S. Krishnan, *Proc. Ind. Ac.*, 1935, **1**, 915.

ation can reach such proportions that we come into the colloidal field." Investigations of association and dissociation in mixtures of liquids must therefore proceed from the simple phenomena which occur in a dilute solution of a polar substance in a non-polar liquid to the manifold phenomena in the field of macroscopic separation (miscibility gaps and colloidal dispersion).

The Association of Alcohols in Non-polar Solvents.

The simplest "molecular separation" (*molekulare Entmischung*), *viz.*, the association to double and triple molecules, can now be easily followed in mixtures of alcohols with non-polar liquids from the dependence of the orientation polarisation on the concentration which explains the arrangement.[10] The diminishing molar polarisation with increasing alcohol concentration (Fig. 1, mol. fraction $c = 0$ to $0{\cdot}05$) corresponds to a non-polar association [11] to double molecules, mainly non-polar, followed at greater concentrations ($c = 0{\cdot}05$ to $0{\cdot}3$) by the appearance of essentially polar triple molecules.[12] Increase of temperature, owing to the better molecular penetration, reduces the association, which shows itself in the greater flatness of the polarisation curve. The substitution of a non-polar, difficultly polarisable solvent by non-polar liquids such as benzene, which in the pure state are "solutions" rather than "mixtures," has an effect similar to that of rise of temperature. Thus the polarisation curve of ethanol in benzene (Fig. 2) is flatter than in other solvents.[13] Cyclohexane, according to previous investigations [14]

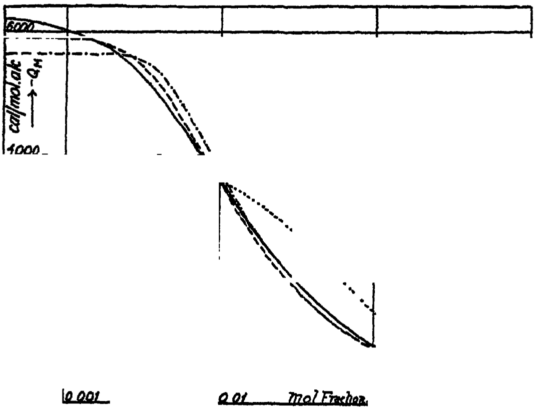

FIG. 3.—Molar heats of mixing (referred to 1 mol. of first-named component).

———— Methanol in cyclohexane.
— — — — Ethanol in cyclohexane.
—·—·— Ethanol in hexane. } 20° C.
. . . . Ethanol in benzene.
—··—·· Benzene in ethanol.

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[10] K. L. Wolf and W. Herold, *Z. physik. Chem. B*, 1934, **27**, 58.

[11] See K. L. Wolf and H. G. Trieschmann, *Z. ges. Nat.*, 1936, **2**, 1.

[12] At still higher concentrations ($c \simeq 0{\cdot}3$), which do not at first interest us here, a further separation to higher associates appears. With the obvious coexistence of several associates of different stoichiometrical compositions, a treatment on the basis of simple stoichiometric proportions no longer has a concrete meaning, particularly since in such strongly "supermolecular mixtures," simple relations, *e.g.*, the law of mass action, should no longer exist, and the definition of the molcular weight loses its simple meaning.

[13] "*Supermolecular* mixtures" approximate to "*molecular mixtures*" with rising temperature. That "molecular solutions" in some ways behave differently from "supermolecular mixtures and solutions" and more like "molecular mixtures" follows from the surface tension values of Trieschmann.[5]

[14] H. G. Trieschmann, *loc. cit.*

and the new measurements with Harms and Frahm,[15] shows the smallest dissociating action. The influence of steric hindrance of the chief association centre (the -OH group) is also shown in the sense of *Entmischung* by the flattening of the polarisation curve with increasing chain length and greater branching of the hydrocarbon chain in the series of isomeric alcohols.[16]

These results lead to a broad understanding of the thermochemical phenomena, as will now be shown by a series of measurements of the heats of mixing.[17] The heat of solution Q_M, referred to a mol. of a component (in the figs. that of the first mentioned component) is smallest when both components, according to the orientation polarisation, are non-polar and of low polarisability and have the smallest dissociating action on dipole-associates (Figs. 3, 4 and $_0Q_M$ values of Table I., which refers to complete molecular penetration in the most dilute solutions or mixtures). The pair cyclohexane-hexane has the lowest values and a linear increase of the heats of mixing (always negative) with increasing dilution, *i.e.*, broadly the molar *heat of dilution* is independent of the concentration (see Fig. 5).

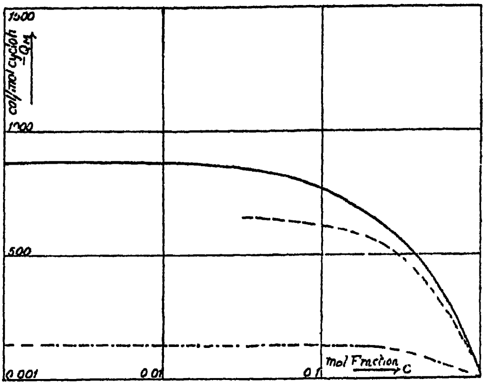

FIG. 4.—Heats of mixing per mol. cyclohexane.

——————— Cyclohexane in benzene.
— — — — — Cyclohexane in ethanol. } 20° C.
— · —— · — Cyclohexane in hexane.

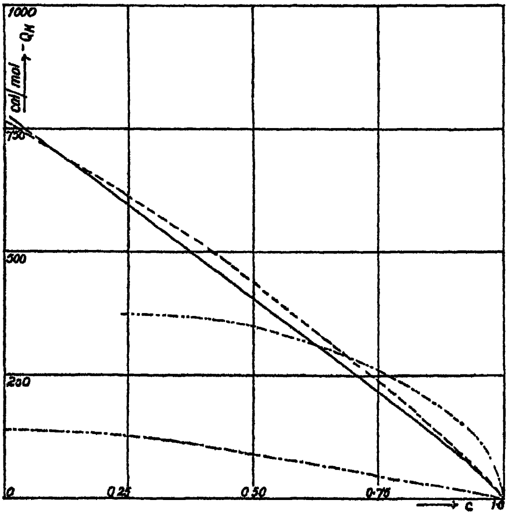

FIG. 5.—Heats of mixing.

— — — — — Benzene in hexane.
——————— Benzene in cyclohexane. } 20° C.
—·——·— Benzene in ethanol.
— · — · — Cyclohexane in hexane.

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[15] Complete accounts of the heats of mixing will appear in Würzbürg, *Diss.*, by H. Frahm, and of the polarisations and exact density measurements in *Diss.*, by H. Harms.

[16] K. L. Wolf (*Z. f. physik. Chem.*, *B*, 1928, **2**, 39); O. Fuchs and K. L. Wolf (*Hand-u. Jahrbuch der chem. Physik*, Vol. 6, I, *B*, 1935); particulars in C. Hennings (*Z. physik. Chem. B*, 1935, **28**, 267) and Müller and Mortier (*Physikal. Z.*, 1935, **36**, 371).

[17] Particulars of our first measurements in *Diss.* by H. Pahlke, Kiel, 1935-36. The apparatus has been further improved and now permits measurements of the temperature dependence of very small heats of solution.

Here a molecular dispersion of the two substances, both of which before mixture behave as "molecular mixtures," is shown at all concentrations. Parallel with the constancy of the heat of dilution is the small and almost linear alteration of the *volume change on mixing*.[18]

TABLE I.—CHANGES OF MOLAR ENERGY AND VOLUME IN THE TRANSFER FROM DILUTE SOLUTIONS TO THE PURE LIQUID (20°).

$-{}_0Q_M$ (cal./Mol.) In	Cyclohexane.	Hexane.	Benzene.	Ethanol.	Methanol.
Cyclohexane .	—	165 ± 20	750 ± 50	5950 ± 100	6300 ± 100
Hexane . .	135 ± 15	—	760 ± 40	5600 ± 50	5650 ± 60
Benzene . .	890 ± 15	1180 ± 80	—	3650 ± 40	3450 ± 40
Ethanol . .	670 ± 20[b]	—	370 ± 10[a]	—	3
Methanol . .	1140[b]	—	—	6[b]	—

${}_mV_M - {}_{fl}V_M$ (cm.^{3}) In	Cyclohexane.	Hexane.	Benzene.	Ethanol.	Methanol.
Cyclohexane .	—	1·0	2·6	> 5	> 7
Hexane . .	0·3	—	1·7	—	—
Benzene . .	2·7	2·0	—	> 2·5	—
Ethanol . .	2·9	—	−1	—	0·03
Methanol . .	4·5	—	—	0·03	—

(a) $c = 0{\cdot}25$; (b) $c = 0{\cdot}05$.

The heat of mixing is quite different when one component, being a polar substance, tends to undergo association, *e.g.*, an alcohol. Here the final values (for the polar substances) tend to be considerable (Table I. and Fig. 3), although the heats of mixing and dilution at great and moderate concentrations of alcohols scarcely differ from those of the cyclohexane-hexane system (Fig. 6). Combining the limiting values of the heats of mixing in hexane and cyclohexane with the heats of vaporisation,[19] it follows that the work required to separate completely the -OH bindings (due essentially to the dipole forces) from the state of pure alcohol to complete dissociation is *ca.* 8 k. cals. per mol. alcohol.

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[18] In the Fig. ΔV is the difference between the volume of the mixture, calculated additively from the densities of the pure liquids, and the volume as calculated from the accurate densities of mixtures; it refers to one mol. of the first-named substance. The values for infinite dilution are given as ${}_mV_M - {}_{fl}V_M$ in Table I.

[19] See K. L. Wolf, H. Pahlke and K. Wehage, *Z. physikal Chem. B*, 1935, 28, 1.

Bearing in mind that the heat of mixing only begins to rise more quickly with increasing dilution at the point at which the polarisation curve has its maximum ($c \gtrsim 0{\cdot}3$)[20] and that it finally rises rapidly at $c = 0{\cdot}05$, where the polarisation has its minimum (Figs. 1, 2, 6, 7) and that corresponding volume changes take place at the same concentrations, we see how completely the conception deduced from the polarisation measurements is borne out, *viz.*, that only in these small concentrations does the "molecular penetration" (dissociation) begin, while at greater concentrations the particles of a "solution" of the super-molecules (*i.e.*, the polymeric alcohol) are mixed with the molecules of a "molecular mixture," *i.e.*, cyclohexane or hexane, to form a super-molecular mixture, in the same way as cyclohexane and hexane are present in the "molecular mixture" cyclohexane-hexane. Besides this qualitative result, it is also possible by means of a combination of measurements to deduce certain quantitative data about *heat effects of the partial processes.* Thus, the concentration dependence of the heat of mixing shows that nearly the full 8 k. cals. (mentioned above as necessary for the dissociation of the -OH groups of the polymeric alcohol) will still be required if the alcohol is already diluted to $c = 0{\cdot}05$. If we assume, in accordance with the polarisation curves, that in concentrations $< c = 0{\cdot}05$ double molecules are dissociating with decreasing concentration, then since 1 mol. (N_L single molecules) should contain ½ mol. of double molecules and the same number of dipole-bonds to start with, we obtain for the work of separation of N_L "bonds" a value of 10 to 16 cals. mol. This value is of the same order as that calculated for a pair of point dipoles with moments of 2×10^{-8} c.g.s. units and a distance of 2Å. Finally we can determine the heat of dissociation of triple molecules, which mainly takes place between $c = 0{\cdot}3$ and $c = 0{\cdot}05$, from the slightly increased

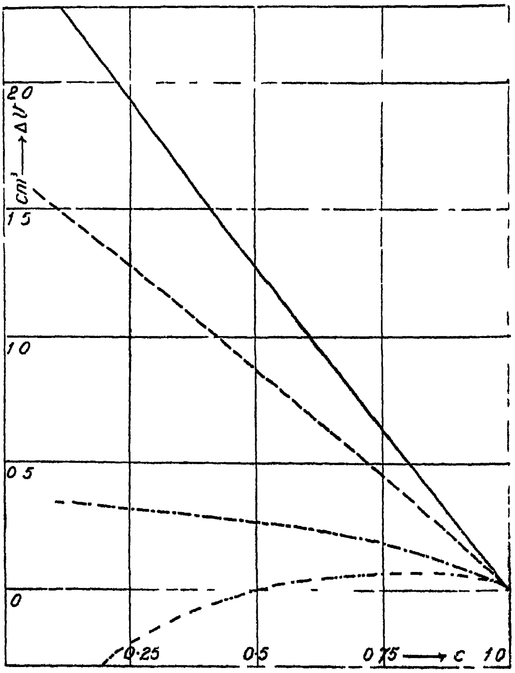

FIG. 5*a*.—Changes of the molar volume of 1 mol. of the first-named component (6° C.).

———— Benzene cyclohexene.
— — — — Benzene hexene.
— · — · — Cyclohexene hexene.
—··—··— Benzol ethanol.
6° C.

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[20] *I.e.*, with ethanol-cyclo hexane, an alcohol concentration which would give rise in the gas to a pressure of about 70 atm.

rise ot the heat of mixing in this region (about 1 k. cal./mol.), if it is supposed that the reaction here is mainly

$$2(\text{Alc.})_3 \leftrightharpoons 3(\text{Alc.})_2.^{21}$$

If, taking ethyl alcohol as a test-substance, we now compare the three non-polar liquids benzene, hexane, cyclohexane, the dissociating action of which, as the polarisation curves show, is in this order, we draw the following conclusions from the heats of mixing. The steepness of the Q_M/c curves, *i.e.*, the dissociating action of the three hydrocarbons used, decreases in the same order (see Fig. 3). The approximate constancy of the heat of mixing, *i.e.*, complete molecular dispersion, is attained in benzene at $c = 0{\cdot}01$, in hexane at $c = 0{\cdot}003$, and in cyclohexane at $c = 0{\cdot}0015$, *i.e.*, complete dissociation is reached when there is 1 molecule of alcohol to 600 cyclohexane, 300 hexane and 100 benzene molecules. We have further found by exact pressure vapour density measurements [22] that at pressures of 200 mm., the vapours of the three hydrocarbons show deviations from the behaviour of the ideal gas, increasing in analogous order. Moreover it is found from measurements of ethanol vapour that the deviation from the behaviour of the ideal gas begins to increase to more than 1 per cent. at 100 mm. pressure and then increases rapidly. Therefore the related ethyl alcohol concentrations required for its dissociation in the vapour and in the three solvents, correspond to vapour pressures of 1800, 600, 300 and 100 mm. The heats of mixing thus lead, in regard to their molecular state, to the same gradation as the measurements of orientation polarisation, volume (*Raümbeanspruchung*), surface tension [5] and internal pressure.[23]

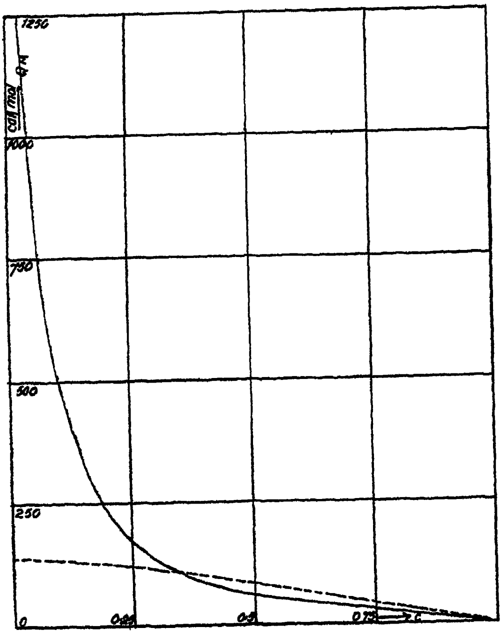

FIG. 6.—Molar heats of mixing.

———— *t*-Butanol in hexane. } 20° C.
— — — Cyclohexane in hexane. } 20° C.

It follows finally from our measurements that the limiting values of the heats of mixing of alcohols in the most dilute solutions in cyclohexane are mainly an expression of the work done against the directional

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[21] Further details in *Diss.* of H. Pahlke. A more precise discussion of the influence of solvation is given by the alcohol-cyclohexane mixtures, see Fig. 3 and *Diss.* by H. Frahm (Würzburg).

[22] The v.p. measurements will be given in full in the Würzburger *Diss.* of E. Steurer.

[23] J. H. Hildebrand, *Solubility* (New York, 1924).

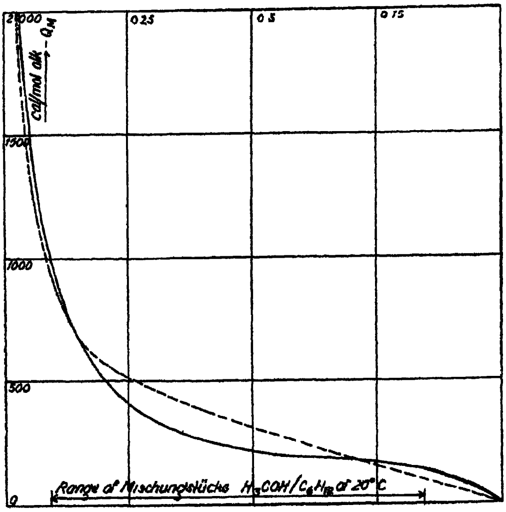

FIG. 7.—Heats of mixing per mol. alcohol.

——— Methanol in cyclohexane. } 20° C.
— — — Ethanol in cyclohexane. }

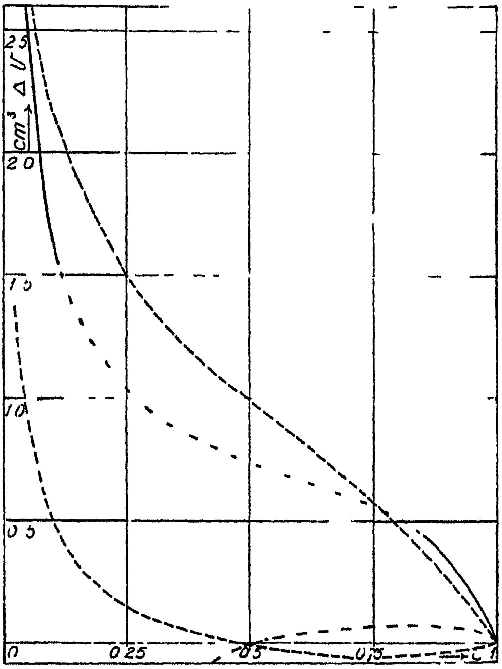

FIG. 7*a*.—Changes of molar volume.

▬▬▬ Methanol cyclohexene. }
▬ ▬ ▬ Ethanol cyclohexene. }
— — — Ethanol benzene. } 6° C.
—·—·· Benzene ethanol. }
- - - - - Not measured. }

forces of the -OH groups, while the smaller values in hexane and, especially, in CS_2 and benzene, are caused by the positive heats of solvation appearing in the "molecular separation" (*molekularen Entmischung*), which with benzene amount to about 4 k. cals. per mol. of -OH. How this solvation action, which corresponds to the formation of a "molecular solution," rather than a "molecular mixture," affects the heats of mixing at different concentrations and the volumes of the solutions can easily be followed in Figs. 1, 5, 5*a*. Further conclusions will be drawn [24] from the measurements of Figs. 3-8. A closer interpretation of the measurements will follow later.

Macroscopic Miscibility Gaps.

With regard to the question of macroscopic miscibility gaps, *e.g.*, of the pair cyclohexane-methanol, our figures show the differences between methanol-cyclohexane and ethanol-cyclohexane at room temperature. Qualitatively however the measurements of the two systems are very similar, probably in agreement with the fact that the ethanol-cyclohexane system also has a miscibility gap at — 18°.

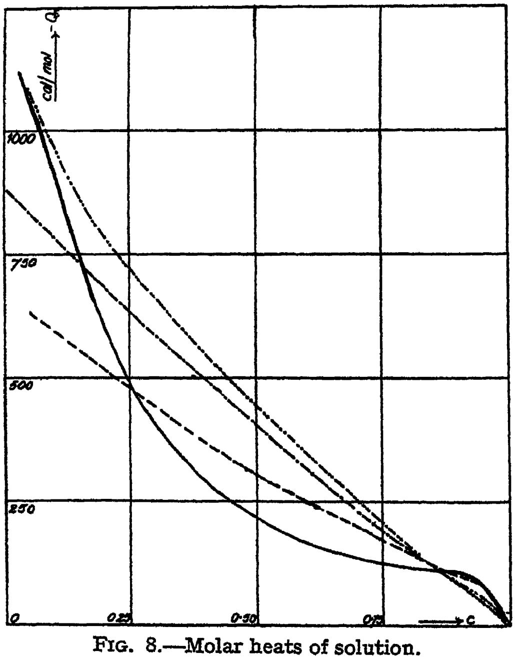

Fig. 8.—Molar heats of solution.

———— Cyclohexane in methanol.
— — — — Cyclohexane in ethanol.
— · — · — Cyclohexane in benzol.
—· ·—· ·— Hexane in benzene.
} 20° C.

The existence of closed miscibility gaps with upper and lower critical temperatures is represented from our point of view as follows. Each liquid behaves, at a sufficiently low temperature (intermolecular energy $< kT$) like a "supermolecular solution," and finally when T is great enough it becomes a "molecular mixture." But while when already "molecularly mixed" (*molekular gemischt*) a liquid must always be miscible with another "molecular mixture" in all proportions, different possibilities occur with "molecular solutions" and "supermolecular solutions and mixtures," according to the shape of the particles and the intermolecular forces. If an unlimited miscibility of two "supermolecular mixtures or solutions" is possible at low temperatures, and if one component becomes a "molecular mixture" quicker than the other at higher temperatures, then we get a partial miscibility beginning at a certain (lower critical) temperature. If finally at still higher temperatures the other component also becomes a "molecular mixture" we get again complete miscibility (higher critical temperature). From this point of view, and from our measurements, we should expect that unsaturated hydrocarbons form miscibility gaps with saturated hydrocarbons at low temperatures; we are examining the pairs benzene-hexane, benzene-cyclohexane; but a first example exists in methane-ethylene. Also the further investigation of the gaps found, with Frahm, at low temperatures with the lower alcohols and CS_2 (see Fig. 9), in connection with calorimetric and density measurements, promises further information regarding the influence of shape and force on macroscopic separations. For the reverse effect, *viz.*, the *increase of miscibility or solubility* by the preparation of a suitable "supermolecular solution," Trieschmann has just found an example (unpublished) which fits in well with the above, by showing that the solubility of NaI in mixtures of *n*-butanol and tertiary butanol with hydrocarbons exhibits a clear parallelism with the degree and kind of association of the alcohol; thus the solubility with rising *n*-butanol content,

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[24] Measurements of the viscosity of the same liquid systems (with H. Rössler, to appear in a Würzburg *Diss.*) and by Snök (*Physikal. Z.*, 1934, **35**, 911) also fit in.

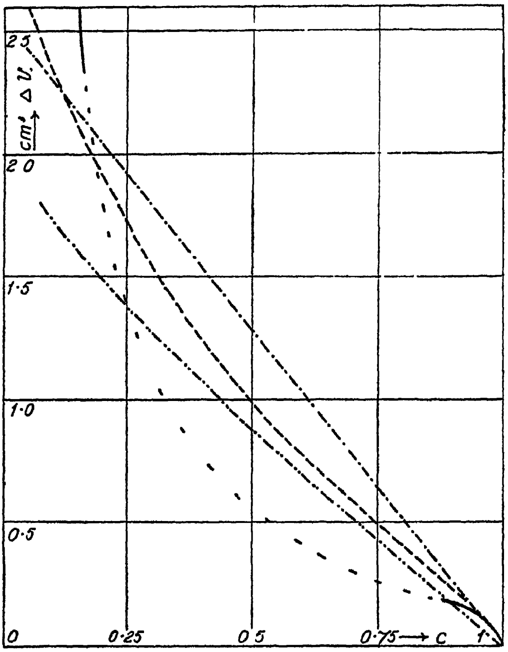

Fig. 8*a*.—Changes of molar volume.

——— Cyclohexane in methanol.
— — — Cyclohexane in ethanol.
— · — · — Cyclohexane in benzene.
—·—··— Hexane in benzene.
╌╌╌╌╌╌ Interpolated.
6° C.

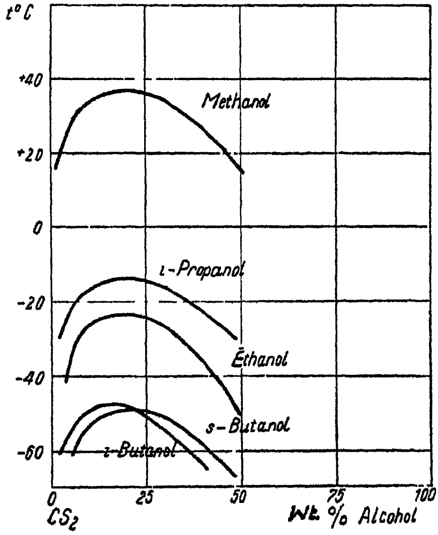

Fig. 9.—Miscibility gaps.

increases strongly between the minimum and the maximum of the polarisation (see Figs. 1 and 2) and decreases later, like the polarisation, at higher alcohol concentrations. With *t*-butanol-hexane this effect does not appear since the minimum and maximum of polarisation are less pronounced. From here we can proceed directly to ternary systems and the phenomena of salting-out. A further application is the question of how the association (*Entmischung*) of the alcohol, up to the full extent of triple molecules, makes itself felt in chemical reactions, *e.g.*, esterification.

We emphasised at the start the counterplay of shape and force in the phenomena of mixture and separation of molecules, atomic aggregations, with the inner structure of which we were not concerned. It is right to point out that this counterplay of shape and force (symmetry and energy) also comes into the question of the inner structure of these aggregates and governs the action of (main or residual) valency. How the system of carbon compounds and of complex compounds presents itself from this point of view does not concern this meeting, but it may be said that the question of shape comes still more into the foreground than with mixtures.

*GENERAL DISCUSSION.**

Professor K. L. Wolf (*Wurzburg*) (*communicated*) : Dr. Butler's report on the different behaviour of alcohols and halides may also be confirmed by measurements of polarisation which accord with the same explanation. Precise measurements carried out in our laboratory by E. Steurer on vapour pressures lead inevitably to the same conclusion, and measurements now being made of the heats of mixing would seem to lead to a final result.

Professor G. Scatchard (*Cambridge, Mass.*) (*communicated*) : The paper of Butler and Harrower gives the impression that the occurrence of the volume fraction rather than the surface fraction in the expression attributed to Hildebrand comes from his assumption that " the polarisation of the whole molecule is located at its centre," which corresponds to the omission of terms higher than $1/r^6$ from London's expressions. The simpler derivation given in my paper[25] shows that this relation need be used only to determine a_{jk} from a_{jj} and a_{kk} by assumption (4). The volume fraction appears through assumption (2), which is not exact for molecules of different sizes or shapes on account of changes in the distributions in the very important region next the central molecule, but it is scarcely to be expected that the error will be compensated by the substitution of surface fractions for volume fractions.

Dr. J. A. V. Butler (*Edinburgh*), in reply, said : The surface fraction appears because all interactions except those between adjacent atoms are neglected. This can only be an approximation, but it seems to me to be a better approximation than that obtained by using London's formula with the assumption that all the polarisability of the molecule is located at its centre. Professor Scatchard remarks that London's expression only comes into his derivation through the relation $a_{jk} = (a_{jj}a_{kk})^{\frac{1}{2}}$. This may hold in London's theory for the interaction of two atoms, but it will not be generally true for the interactions of two complex molecules except when their distance apart is large compared with their dimensions. At short distances it would be necessary to consider the distribution of the polarisability within the molecules and the proper interaction energy will be obtained by summing the interactions of the various elements of polarisability in the two molecules, to which my derivation is an approximation.

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* On the two preceding papers.

[25] *This vol.*, p. 160.

DIPOLE INTERACTION IN MIXTURES OF BENZENE WITH SOME OF ITS POLAR DERIVATIVES.

BY A. R. MARTIN.

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Intermolecular attraction in liquids arises from van der Waals or dispersion forces, electrostatic interaction of dipoles, and perhaps in certain cases, notably in hydroxylic compounds, chemical co-ordination. But it is possible that the exceptionally strong intermolecular forces for which co-ordination has been invoked as an explanation are dipole attractions made unusually powerful by the geometry of the molecules in which they occur.[1, 2, 3] In order to investigate this possibility, the partial vapour pressures and dielectric constants of mixtures of benzene with a number of its polar derivatives, including the hydroxylic compounds benzyl alcohol and phenol, have been studied.[1, 3, 4] The close similarity of these liquids to benzene, apart from the groups carrying the dipoles, might be expected largely to eliminate the effect of dispersion forces. However, before any conclusion can be drawn from the results, it is necessary to have some calculation of the contribution of dipole interaction to the free energy of the mixture.

Calculation by the methods of statistical mechanics is difficult, and the results are applicable only to dilute solutions.[5, 6] Another method is to consider one dipole and represent the remainder of the mixture as a continuous medium of dielectric constant equal to the observed value for that mixture.[3, 16] The other dipoles enter in by their determination of the dielectric constant of the medium. The free energy of transferring the dipole from any mixture to a chosen standard state is given by the difference in its electrostatic energy in the two media. Assuming that in the absence of dipole interaction activity is proportional to molar fraction, this can be equated to $-kT \ln a/N$, where a is the activity of the dipolar substance in a mixture in which its molar fraction is N, k is the gas constant per molecule, and T the absolute temperature. The earlier calculations of the electrostatic energy[7, 8] contained some errors, but the calculation of Kirkwood[9] is correct. Using Kirkwood's value for the electrostatic energy, we have

$$-kT \ln \frac{a}{N} = \frac{\mu^2}{d^3}\left\{\frac{D-1}{2D+1} - \frac{D_s-1}{2D_s+1}\right\} \quad . \quad . \quad (1)$$

where μ is the dipole moment, d the molecular radius, D the dielectric constant of the mixture N, and D_s the dielectric constant of the standard

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[1] Martin and Collie, *J. Chem. Soc.*, 1932, 2665.

[2] Bernal and Fowler, *J. Chem. Physics*, 1933, 1, 515.

[3] Martin, *Trans. Faraday Soc.*, 1934, 30, 759

[4] Martin and George, *J. Chem. Soc.*, 1933, 1413.

[5] Debye, *Handbuch Radiologie*, 1925, 6, 638.

[6] Fuoss, *J. Amer. Chem. Soc.*, 1934, 56, 1027.

[7] Martin, *Phil. Mag.*, 1929, 8, 547.

[8] Bell, *J. Chem. Soc.*, 1931, 1371; *Trans. Faraday Soc.*, 1931, 27, 797.

[9] Kirkwood, *J. Chem. Physics*, 1934, 2, 351.

state. A more detailed account of the calculation will not be given, since it has recently been the subject of a critical study by R. P. Bell.[10]

Experimental.

The partial vapour pressure measurements have been reported elsewhere.[1, 4] However, a few of the earliest measurements have been repeated with the results given in Table I. The new chlorobenzene-benzene figures confirm the old ones, but the bromobenzene-benzene results differ and should be regarded as superseding those previously published. Under $N_{mixt.}$ and $N_{dist.}$ are the molar fractions of the polar component in the mixture and distillate; P denotes the total pressure, and p the partial pressure of the polar component in millimetres; the temperature is 70°.

TABLE I.

$N_{mixt.}$	$N_{dist.}$	P.	p.
Chlorobenzene-Benzene Mixtures.			
0·0252	0·0052	530·5	2·76
0·0764	0·0167	503·5	8·40
0·1034	0·0234	491·1	11·43
Bromobenzene-Benzene Mixtures.			
0·0146	0·00143	536·6	0·77
0·0284	0·00285	527·1	1·50
0·0555	0·00567	511·6	2·90
0·1285	0·01341	472·0	6·34

Of the dielectric constants only a few preliminary figures have appeared.[3] An account of the dielectric constant measurements will therefore be given. Although some measurements were made by a heterodyne method, a resonance method was finally adopted, since it was less sensitive to power loss in the experimental condenser. It was found that a frequency of 180 kc. was a satisfactory compromise between the claims of a high and low frequency. The circuit is given in Fig. 1. The valve V_1 of the oscillator was an AC/SG Mazda, with anode potential of zero, screening grid potential of + 95 volts, and grid and filament potentials of − 25 volts. The capacity C_1 was a Sullivan "second grade" mica condenser of the fixed value 0·002 μF, and the inductance L_1 a Sullivan-Griffiths "second grade standard" coil constructed on the temperature compensation principle, value 391 μH. The frequency of the oscillator was perfectly steady. The resonating circuit consisted of a similar coil L_2, value 352·7 μH, and the standard condensers C_2, C_3, C_4 and the experimental condenser C_5. C_4 was a variable air condenser, maximum value 640 $\mu\mu$F, and C_2 and C_3 were fixed air condensers of values 500 and 1000 $\mu\mu$F for extending the range of the variable. The oscillator and the resonating circuit

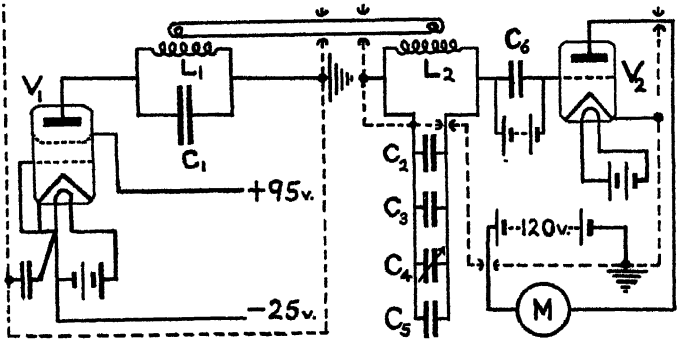

FIG. 1.

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[10] Bell, *Trans. Faraday Soc.*, 1935, 31, 1557.

were lightly coupled by two turns of wire of about the same diameter as the coils L_1 and L_2 held about 6 cms. from them. Resonance was detected by an anode-bend detector. The Mazda AC/HL valve, V_2, had an anode potential of 120 volts and an adjustable negative bias on the grid (max. 9 volts). The capacity of the mica condenser C_6 was 0·0005 μF. The dotted lines indicate earthed brass boxes; the coupling leads between the oscillator and the resonating circuit and from the detector to the milliammeter M were also shielded. A pair of settings of the variable condenser which gave the same reading on each side of the resonance point were found. The difference between the means of such pairs of settings with the experimental condenser connected and disconnected gave its capacity.

TABLE II.

N.	*D.*	Dens.	$P_A+0.$
Pure Benzene.			
0·0000	2·193	0·8246	—
Benzyl Alcohol-Benzene Mixtures.			
0·0000	—	—	52·0
0·1974	3·039	0·8663	57·0
0·3766	4·163	0·9020	58·2
0·4950	4·961	0·9238	55·9
0·6524	6·277	0·9514	53·7
0·7720	7·327	0·9718	51·3
1·0000	9·467	1·0062	47·1
Phenol-Benzene Mixtures.			
0·0000	—	—	43·3
0·1074	2·540	0·8475	45·7
0·1346	2·639	0·8534	45·9
0·2017	2·934	0·8681	47·6
0·2033	2·943	0·8680	47·8
0·3246	3·567	0·8942	48·5
0·4072	4·063	0·9119	48·1
0·4545	4·375	0·9215	47·8
0·5996	5·458	0·9520	46·1
0·7257	6·517	0·9781	42·1
1·0000	9·161	1·0307	39·0
Benzonitrile-Benzene Mixtures.			
0·0000	—	—	273·6
0·2068	6·118	0·8584	161·0
0·3778	9·449	0·8834	117·8
0·5968	13·75	0·9127	88·7
0·7818	17·30	0·9358	73·8
1·0000	21·60	0·9600	62·4
Nitrobenzene-Benzene Mixtures.			
0·0000	—	—	282·7
0·1876	5·867	0·8957	169·5
0·3950	10·524	0·9686	116·7
0·6059	15·92	1·0373	89·6
0·7803	20·81	1·0906	75·5
1·0000	27·59	1·1533	63·5
Chlorobenzene-Benzene Mixtures.			
0·0000	—	—	43·8
0·2846	2·983	0·8954	38·6
0·5664	3·760	0·9466	35·7
0·8783	4·591	1·0275	30·7
1·0000	4·942	1·0521	29·8
Bromobenzene-Benzene Mixtures.			
0·0000	—	—	43·0
0·1613	2·648	0·9360	39·4
0·4126	3·335	1·0970	34·9
0·6563	3·962	1·2129	31·3
0·7955	4·300	1·3191	29·6
1·0000	4·783	1·4270	27·6
Aniline-Benzene Mixtures.			
0·0000	—	—	43·2
0·1803	2·725	0·8548	38·6
0·3775	3·413	0·8867	36·8
0·5968	4·250	0·9206	33·9
0·7934	5·053	0·9494	31·3
1·0000	5·932	0·9783	28·9
Dimethylaniline-Benzene Mixtures.			
0·2292	2·836	0·8522	39·8
0·3606	3·169	0·8656	37·6
0·6055	3·733	0·8873	34·3
0·8021	4·099	0·9018	32·0
1·0000	4·423	0·9152	30·0
Anisole-Benzene Mixtures.			
0·0000	—	—	28·8
0·1981	2·547	0·8534	27·4
0·3906	2·892	0·8789	26·4
0·6320	3·306	0·9078	25·1
0·6659	3·348	0·9116	24·7
1·0000	3·887	0·9465	23·3

In the experimental condenser (Sayce and Briscoe,[11] Ball,[12] and Sugden [13]) the plates consisted of two films of silver deposited on concentric glass tubes. The outer silver layer was earthed, and the condenser was put in circuit by lowering the lead in the inner glass tube, which was connected

TABLE III.

Benzyl Alcohol-Benzene Mixtures (p_s, N = 0, 11·8).

N.	D.	p.	$\frac{D-1}{2D+1}$.	a/N (inf. diln.)	a/N (pure liq.)
0·1	2·60	0·97	0·258	0·822	4·620
0·2	3·075	1·35	0·290	0·5725	3·215
0·3	3·64	1·58	0·319	0·4465	2·510
0·4	4·30	1·70	0·344	0·360	2·023
0·5	5·03	1·80	0·365	0·305	1·714
0·6	5·84	1·90	0·382	0·2783	1·508
0·7	6·69	1·95	0·3955	0·236	1·326
0·8	7·575	2·00	0·407	0·2118	1·190
0·9	8·50	2·05	0·4165	0·193	1·084
1·0	9·467	2·10	0·425	0·178	1·000

Phenol-Benzene Mixtures (p_s, N = 0, 26·9).

N.	D.	p.	$\frac{D-1}{2D+1}$.	a/N (inf. diln.)	a/N (pure liq.)
0·1	2·500	2·40	0·250	0·893	2·927
0·2	2·930	3·40	0·2815	0·6325	2·073
0·3	3·430	4·13	0·309	0·512	1·678
0·4	4·010	4·87	0·334	0·4525	1·484
0·5	4·700	5·57	0·356	0·414	1·358
0·6	5·460	6·15	0·374	0·381	1·250
0·7	6·300	6·70	0·3895	0·356	1·167
0·8	7·400	7·20	0·405	0·3345	1·097
0·9	8·160	7·70	0·4135	0·3175	1·043
1·0	9·161	8·20	0·4225	0·305	1·000

Benzonitrile-Benzene Mixtures (p_s, N = 0, 18·8).

N.	D.	p.	$\frac{D-1}{2D+1}$.	a/N (inf. diln.)	a/N (pure liq.)
0·1	4·08	1·88	0·336	1·000	1·790
0·2	6·00	3·30	0·385	0·878	1·571
0·3	7·95	4·47	0·411	0·793	1·418
0·4	9·90	5·73	0·428	0·7615	1·363
0·5	11·83	6·80	0·439	0·724	1·294
0·6	13·75	7·90	0·448	0·700	1·254
0·7	15·70	8·73	0·454	0·6635	1·187
0·8	17·65	9·43	0·459	0·6275	1·123
0·9	19·60	10·02	0·463	0·593	1·060
1·0	21·60	10·50	0·466	0·559	1·000

Nitrobenzene-Benzene Mixtures (p_s, N = 0, 7·80).

N.	D.	p.	$\frac{D-1}{2D+1}$.	a/N (inf. diln.)	a/N (pure liq.)
0·1	4·10	0·78	0·339	1·0000	1·515
0·2	6·13	1·56	0·387	1·0000	1·515
0·3	8·30	2·14	0·415	0·914	1·385
0·4	10·64	2·69	0·432	0·862	1·305
0·5	13·13	3·18	0·445	0·816	1·235
0·6	15·75	3·59	0·454	0·7675	1·160
0·7	18·52	4·01	0·461	0·7345	1·1125
0·8	21·44	4·41	0·466	0·707	1·070
0·9	24·43	4·79	0·470	0·682	1·032
1·0	27·59	5·15	0·473	0·660	1·000

Chlorobenzene-Benzene Mixtures (p_s, N = 0, 114·3).

N.	D.	p.	$\frac{D-1}{2D+1}$.	a/N (Inf. diln.)	a/N (pure liq.)
0·1	2·473	11·5	0·248	1·000	1·158
0·2	2·750	23·0	0·269	1·000	1·158
0·3	3·025	34·0	0·287	0·993	1·143
0·4	3·300	43·8	0·303	0·958	1·103
0·5	3·575	53·7	0·316	0·939	1·081
0·6	3·847	63·1	0·327	0·920	1·059
0·7	4·125	72·7	0·338	0·908	1·046
0·8	4·387	82·1	0·347	0·898	1·033
0·9	4·660	91·3	0·355	0·8875	1·021
1·0	4·942	99·3	0·363	0·868	1·000

Bromobenzene Benzene Mixtures (p_s, N = 0, 50·0).

N.	D.	p.	$\frac{D-1}{2D+1}$.	a/N (Inf. diln.)	a/N (pure liq.)
0·1	2·473	5·0	0·248	1·000	1·149
0·2	2·758	10·0	0·270	1·000	1·149
0·3	3·032	15·0	0·287	1·000	1·149
0·4	3·300	20·0	0·303	1·000	1·149
0·5	3·562	24·0	0·315	0·960	1·103
0·6	3·813	27·9	0·326	0·930	1·068
0·7	4·067	31·9	0·336	0·912	1·0475
0·8	4·307	35·8	0·344	0·895	1·028
0·9	4·548	39·7	0·351	0·883	1·013
1·0	4·783	43·5	0·358	0·870	1·000

Aniline-Benzene Mixtures (p_s, N = 0, 17.0).

N.	D.	p.	$\frac{D-1}{2D+1}$.	a/N (Inf. diln.)	a/N (pure liq.)
0·1	2·470	1·70	0·248	1·000	1·619
0·2	2·790	3·33	0·272	0·980	1·584
0·3	3·128	4·70	0·293	0·922	1·492
0·4	3·500	5·85	0·3125	0·862	1·392
0·5	3·878	6·75	0·328	0·7945	1·286
0·6	4·260	7·55	0·343	0·740	1·198
0·7	4·660	8·35	0·355	0·702	1·136
0·8	5·073	9·10	0·366	0·669	1·083
0·9	5·498	9·85	0·377	0·644	1·041
1·0	5·932	10·50	0·383	0·618	1·000

Anisole-Benzene Mixtures (p_s, N = 0, 53·8).

N.	D.	p.	$\frac{D-1}{2D+1}$.	a/N (Inf. diln.)	a/N (pure liq.)
0·1	2·373	5·38	0·239	1·000	1·345
0·2	2·550	10·76	0·254	1·000	1·345
0·3	2·730	15·40	0·268	0·955	1·283
0·4	2·902	19·60	0·279	0·912	1·225
0·5	3·079	23·40	0·291	0·871	1·170
0·6	3·248	26·92	0·300	0·833	1·120
0·7	3·413	30·28	0·308	0·805	1·081
0·8	3·579	33·60	0·316	0·781	1·050
0·9	3·733	36·80	0·323	0·760	1·0225
1·0	3·887	40·00	0·329	0·744	1·000

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[11] Sayce and Briscoe, *J. Chem. Soc.*, 1925, **127**, 315.

[12] Ball, *ibid.*, 1930, 570.

[13] Sugden, *ibid.*, 1933, 768.

with the inner silver layer through mercury and a platinum wire sealed through the glass. The experimental condenser was immersed in a paraffin bath, maintained at 70°.[13] All metal parts were earthed. The experimental condenser was calibrated with air and benzene as dielectrics. Its air capacity was 65·7 $\mu\mu$F. The benzene was purified by the method of Richards and Shipley,[14] and the value $D_{25} = 2 \cdot 272$ assumed. The other liquids were purified as previously described.[1, 4] In the cases of a few pure liquids a correction was applied for conductivity as given by Sugden ;[13] it never amounted to more than 3 parts in 1000. As a check on the accuracy the dielectric constant of benzonitrile at 25° was found to be 25·23 compared with Sugden's value of 25·19 ± 0·04, and that of nitrobenzene at 70° 27·59 compared with the value 27·64 interpolated from Ball's figures. The heterodyne method used in the earlier measurements gave a value for the dielectric constant of chlorobenzene at 25° of 5·615 compared with Sugden's value of 5·612 ± 0·006.

In order to obtain the molar polarisations, the densities at 70° were measured in pyknometers fitted with ground-glass caps.

The results are recorded in Table II. ; they all refer to a temperature of 70°. Under N is given the molar fraction of the polar component, under D the dielectric constant, under *dens.* the density, and under P_{A+0} the sum of the molar orientation and atomic polarisation of the polar substance. Values of P_{A+0} at $N = 0$, calculated from the dipole moments, are also given.

In Table III. are the partial vapour pressures of the polar components (p) and the corresponding values of the dielectric constant interpolated graphically from the data already reported. Values of a/N are given both for the standard state that of the pure liquid, $a/N_{\text{pure liq.}}$, and for the standard state an infinitely dilute solution in benzene, $a/N_{\text{inf. diln.}}$, obtained by drawing the tangent to the graph of p against N in the limit where N tends to zero; the value of p given by this tangent at $N = 1$ is denoted by p_s, $N = 0$.

Discussion.

Equation (1) demands a linear relation between $-\log_{10} a/N$ and $\dfrac{D-1}{2D+1}$. In general, the data in Table III. satisfy this demand except those for mixtures of low dielectric constant, as has been anticipated on theoretical grounds by Bell.[10] Some typical graphs are illustrated in Fig. 2. From the slope of a straight line it is possible, knowing the dipole moment, to calculate d, the molecular radius. The results of this calculation are given in Table IV., using both $-\log_{10} a/N_{(\text{inf. diln.})}$ and $-\log_{10} a/N_{(\text{pure liq.})}$, the corresponding values of d being denoted by d_1 and d_2 respectively. The values of the molecular radius (r) derived from the molecular volumes at 25° (for phenol at 70°) on the assumption that the liquid consists of close-packed spheres ($r = 0 \cdot 665 \times 10^{-8} \times \sqrt[3]{V_m}$) are also given.

TABLE IV.

	μ (Debyes).	d_1 cms. $\times 10^8$.	d_2 cms. $\times 10^8$.	r cms. $\times 10^8$.
Benzyl alcohol	1·70	1·91	1·93	3·12
Phenol . .	1·50	2·18	2·18	3·00
Benzonitrile .	3·90	2·90	2·95	3·12
Nitrobenzene .	3·95	3·43	3·55	3·12
Chlorobenzene	1·56	3·04	3·09	3·11
Bromobenzene	1·55	2·89	2·90	3·14
Aniline . .	1·55	2·25	2·26	3·00
Anisole . .	1·27	2·08	2·10	3·18

For each substance the values of d are practically identical, as also are the ranges of validity of the linear relation. This affords a check on the reliability of the data. The results will now be considered in detail for each substance.

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[14] Richards and Shipley, *J. Amer. Chem. Soc.*, 1919, 41, 2007.

In the case of benzyl alcohol the linear relation between $-\log a/N$ and $\frac{D-1}{2D+1}$ holds over practically the entire range of composition with no hint of a systematic deviation. The value of *d* is reasonable but smaller than for most of the other substances, corresponding to the smallness and the relatively unshielded position of the hydroxyl dipole, to which the strong association of benzyl alcohol is due. It appears impossible to resist the conclusion that here dipole interaction is the predominating influence, and that the assumption of any special kind of intermolecular force such as co-ordination is unnecessary. The general significance of the results for the other hydroxylic substance, phenol, is the same. The points lie on an unequivocal straight line over the range of molar fraction 1·0 to 0·25 (dielectric constant 9·16 to 3·2),below which they deviate. The value of *d* is slightly larger than for benzyl alcohol, owing to the somewhat less exposed position of the hydroxyl group.

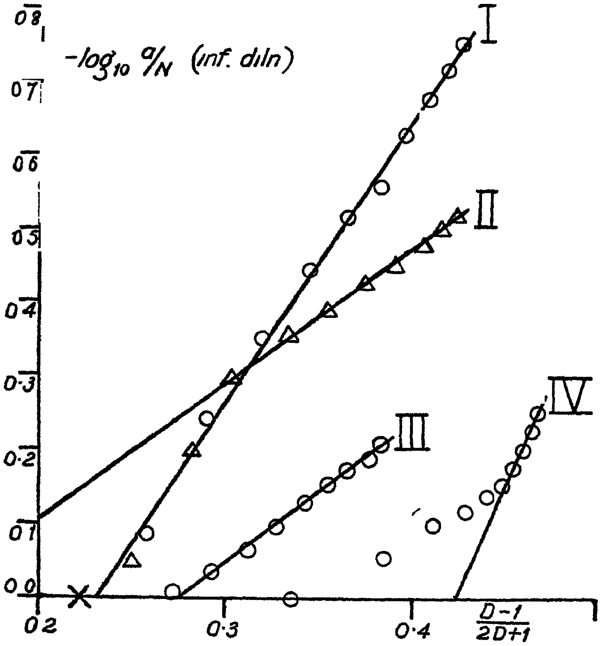

FIG. 2.

I. Benzyl Alcohol. III. Aniline.
II. Phenol. IV. Benzonitrile.
× = value of $\frac{D-1}{2D+1}$ for pure benzene.

The linear relation holds only in mixtures of dielectric constant higher than about 13·5 (molar fraction 0·5 or 0·6) for the substances with large dipole moments, benzonitrile and nitrobenzene. This is about the dielectric constant below which it would be expected to fail for substances with $\mu = 3{\cdot}9$ Debyes and $d = 3$Å, according to Bell.[10] In spite of their large dipole moments, benzonitrile and nitrobenzene are far from being the most strongly associated of the substances investigated, and accordingly for them d is fairly large; this may be attributed to the fact that one end of the dipole is well shielded by the benzene nucleus.

The value of d for chlorobenzene is bigger than it is for bromobenzene, although bromine is undoubtedly larger than chlorine. This curious result is probably due to the neglect of dispersion forces. The larger dispersion forces in bromobenzene to a certain extent compensate for the smaller dipole interaction due to the greater screening of the dipole. The ranges of validity of the linear relation between $-\log a/N$ and $\frac{D-1}{2D+1}$ for these two substances from dielectric constants of about 3·7 to 4·9 (corresponding to molar fractions of 0·5 and 0·6 to 1·0) are inevitably not great owing to the low dielectric constants of the pure substances; but they might be expected to extend to somewhat lower dielectric constants for substances of such low dipole moment. Such straight lines as are obtained cannot, therefore, be regarded as indicating the predominance of dipole interaction amongst the intermolecular forces. The conclusion that dispersion forces are comparable in influence to dipole interaction in these mixtures is supported by a comparison of the partial vapour pressures of chlorobenzene and *p*-dichlorobenzene in mixtures with benzene.[4]

With aniline a good straight line is obtained from a molar fraction of 0·3 (dielectric constant 3·0) upwards. The value of d is reasonable, and there appears to be no hint of co-ordination, which has been held to occur to a slight extent in this substance. The deviations of the partial vapour pressures of dimethylaniline from the ideal are too near the rather large experimental error to be suitable for theoretical treatment.

For anisole there is a good straight line above a molar fraction of 0·6, although the deviations below this concentration are not large. The value of d is smaller than for phenol; this is probably due to neglect of the difference between the dispersion forces arising from CH_3 and H.

The decrease of molar polarisation with concentration shown by most non-hydroxylic polar substances has often been attributed to progressive association to form double molecules of zero dipole moment. Although there is sometimes a parallelism between the degree of association derived from polarisations and from freezing-point determinations, the law of mass action, at least in its simplest form, does not apply to the association.[15] In general, there is not agreement between the degrees of association derived from the polarisations reported here and from the vapour pressures (on the assumption that the double molecules are non-volatile); and the law of mass action holds in neither case. The molar polarisation of both phenol and benzyl alcohol at first increases with concentration and then decreases.

My thanks are due to Imperial Chemical Industries, Ltd., for a grant for the dieletric constant apparatus.

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[15] Davy and Sidgwick, *J. Chem. Soc.*, 1933, 281.
[16] Martin, *Nature*, 1931, 128, 456.

Summary.

Partial vapour pressures and dielectric constants of mixtures of benzene with some of its polar derivatives have been reported. Dipole interaction suffices to account for the strong association of the hydroxylic compounds. Where the dipole is well shielded or very small, it is necessarv to take into account dispersion forces as well.

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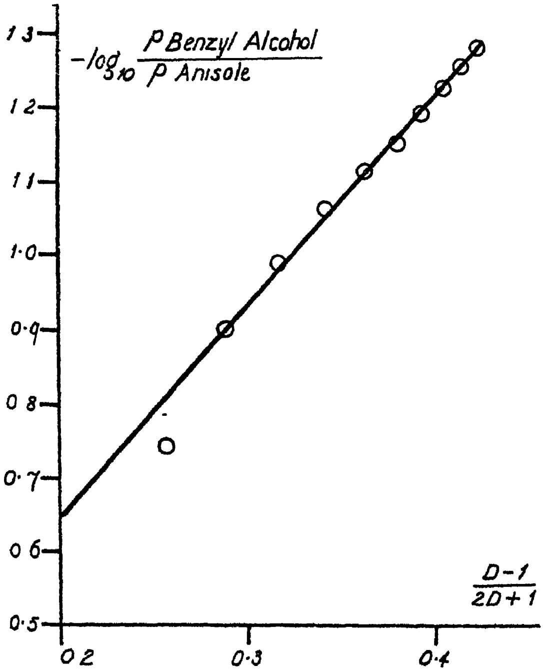
GENERAL DISCUSSION.

Dr. A. R. Martin (*London*), in introducing his paper, added : Benzyl alcohol and anisole are isomeric (C_7H_8O). It is therefore not unreasonable to suppose that in these two substances the dispersion forces are the same. Let it further be assumed that the small and not very exposed dipole of anisole is without effect on the intermolecular forces (this assumption is supported by a comparison of the values of d for anisole and phenol, see above). A comparison of the partial vapour pressures of benzyl alcohol and anisole at the same molar fractions will then eliminate the effect of dispersion forces in the former compound. Since the formation of the hydroxyl dipole in C_7H_8O results in the acquisition by the medium of the dielectric constant of the benzyl alcohol mixture and the polarity of anisole is neglected, we should have :—



$$-kT\ln\frac{p_{\text{Benzyl Alcohol}}}{p_{\text{Anisole}}} = \frac{\mu^2}{d^3}\left(\frac{D-1}{2D+1}\right) + const.$$

where D = the dielectric constant of the benzyl alcohol-benzene mixture,
μ = the dipole moment of benzyl alcohol (1·70 Debyes),
and d = the molecular radius of benzyl alcohol.

The results of this calculation are illustrated in the diagram, where $-kT\log\frac{p_{\text{Benzyl Alcohol}}}{p_{\text{Anisole}}}$ is plotted against $\frac{D-1}{2D+1}$ for molar fractions ranging from 0·1 to 1·0 at intervals of 0·1. The slope of the line gives $d = 2{\cdot}12 \times 10^{-8}$ cms.

The neglect of the polarity of anisole raises the value of *d*. In the calculation of *d* for benzyl alcohol from the data for benzyl alcohol-benzene mixtures alone, the neglect of dispersion forces diminishes its value. The agreement between the values of *d* calculated by the two methods (2·12 and 1·92 Å.) therefore confirms the conclusions that the association of benzyl alcohol is chiefly due to the interaction of hydroxyl dipoles and that in anisole dispersion forces are the more important.

There remains the question, what molecular picture does the treatment of dipole interaction by means of the electrostatic energy of a dipole in media of given dielectric constant imply ? The two fundamental assumptions of the treatment are that (1) the average distribution of dipoles around the central dipole is similar to that at the plates of the condenser used to measure the dielectric constant (use of macroscopic dielectric constant and neglect of electrical saturation), and (2) the central dipole might be any dipole. The substitution of a continuous medium for a discontinuous one is probably justified by the fact that one is dealing with an average effect. There will be on the average more − ve poles than + ve around a + ve pole, and *vice versa*. This implies a certain degree of structure, but one scarcely more rigid than that of a dilute solution of a strong electrolyte. In the liquids dealt with here, at any rate, it is apparently unnecessary to consider a distribution of charge more detailed than the dipole.

Dr. J. A. V. Butler (*Edinburgh*) said : It must be admitted that Martin's equation gives very good agreement with the variation of the activity coefficient with the dielectric constant. The question remains however, whether the simple dipole interactions on which the derivation is based are a reasonable interpretation of the physical state of the solution. This question may be put in another form by asking whether the constant of the equation is really μ^2/d^3. I would like to suggest that a crucial test might be obtained by similar measurements over a range of temperature. The " entropy of association " of the alcohols shows that the activity coefficient in a given solution varies rapidly with the temperature. Could this be accounted for in terms of the temperature variation of the dielectric constant, using a constant value of the dipole radius *d* ?

Dr. R. J. B. Marsden (*Manchester*) doubted if Dr. Martin's assumption that the phenyl nucleus of a substituted benzene was strictly similar or fairly comparable to the surrounding unsubstituted solvent benzene molecules was justified, in view of the great polarisibility of benzene and the chemical directive effects of the substituents, in particular the − OH group which is a most powerful *o*- and *p*-directing group. This objection appears to be borne out by Dr. Martin's results, the curve obtained for benzyl alcohol being " normal," the directive effect of the − OH group in this molecule being largely blocked by the saturated − CH_2-group. In view of these facts the question is raised as to how far the author's conclusions are valid. The use of *cyclo*-hexane and substituted *cyclo*-hexanes would have been a happier choice of materials.

(*Communicated*)—Professor Errera has suggested that the differences between the moments of series of alkyl and aryl compounds would not affect Dr. Martin's argument, but this surely overlooks the fact that it is just these differences when the absolute direction of the moments is taken into account which have been shown by Sutton [17] to be very closely connected with the directive powers of substituents mentioned in the original comment.

It is also of interest to note that in Fig. 2 that when the curve II. for phenol departs from its original direction it appears to fall along the curve I. for benzyl alcohol.

Dr. A. R. Martin (*London*) said : In reply to Dr. Marsden, electromeric disturbances in the benzene ring are probably slight in the absence of substances with which chemical reaction occurs. However, the applicability of the linear relation between $-\log a/N$ and $\frac{D-1}{2D+1}$ shows that, even if such disturbances do occur to a certain extent, they are allowed for by the value of μ^2/d^3, and the conclusion that the marked association of benzyl alcohol and phenol is due to electrostatic forces of a dipolar character stands.

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[17] *Proc. Roy. Soc., A.*, 1931, **133**, 668.

THE STRUCTURE OF SOME MOLECULAR COMPLEXES IN THE LIQUID PHASE.

By SAMUEL GLASSTONE.

Received 5th August, 1936.

An important cause of deviation from ideal behaviour in liquid mixtures is the formation of complexes between the two components, and two points of view have in general been held concerning the structure of such complexes. The molecules may be held together by definite chemical forces involving a co-ordinate link, or the forces may be of a physical nature due to dipole association. It will be seen later that it is doubtful whether it is always possible to draw a clear distinction between the two types of complex formation, but it is desirable to enquire if there are any lines of evidence which favour definitely one point of view or the other. The work of Hammick and Sixsmith [1] on the rate of compound formation between a nitro-derivative and a hydrocarbon suggests that, at least in the case studied, true chemical combination occurs, and it appeared that further information might be obtainable from an examination of the dielectric polarisations of certain mixtures in which there was good reason to suppose that complex formation occurred between the constituents. Mixtures of diethyl ether, or acetone, with chloroform are well known to be abnormal, especially in so far as vapour pressures and viscosities [2] are concerned, and hence a study was made of the dielectric polarisations of a series of mixtures in which one of the components was an ether or acetone and the other was a trihalogenomethane or a related substance. Although mixtures of acetone and carbon tetrachloride give vapour pressure curves which do not deviate abnormally from ideal behaviour, they form solid compounds [3] and consequently liquid systems of this type appeared worthy of investigation: carbon tetrachloride and tetrabromide and hexachloroethane were studied with ethers or with acetone. Quinoline forms a well-defined crystalline compound with iodoform [4] having the formula $CHI_3 . 3C_9H_7N$, which suggests some kind of association between each molecule of quinoline and an atom of iodine: the dielectric polarisations of mixtures of tri- and tetra-halogenomethanes with quinoline have, therefore, been measured and important conclusions drawn from the results.

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[1] Hammick and Sixsmith, *J. Chem. Soc.*, 1935, 580.

[2] *Cf.* Schultze, *Z. physikal. Chem.*, 1919, **93**, 370; Macleod, *Trans. Faraday Soc.*, 1934, **30**, 482.

[3] Wyatt, *Trans. Faraday Soc.*, 1929, **25**, 43.

[4] Rhoussopoulos, *Ber.*, 1883, **16**, 202.

Experimental.

For each system a number of mixtures was made up and the dielectric constant, refractive index and density measured ;[5] the total polarisation of each mixture was then calculated in the usual manner. From the result the molar polarisation of each component was evaluated by assuming that of the other to be equal to its value in the pure state and to remain constant throughout the whole series of mixtures. The results for the ether–chloroform system are shown in the figure, the corresponding curves for mixtures of each component with the non-polar solvent *cyclo*hexane being given for comparison. It will be seen that not only is the molar polarisation of each component in the ether–chloroform mixture greater than in *cyclo*hexane, but there is a rapid increase as infinite dilution is approached. The abnormal polarisation must be attributed to the fact that the dipole moment of each constituent is greater than its usual value as a result of association with the other in the complex, and the rapid increase as infinite dilution is attained is to be expected if the law of mass action applies to the system. It can be shown by a simple calculation, which does not involve any assumptions as to the nature of the complex, that when two molecular species A and B form a complex AB in solution the dielectric polarisation of the latter may be obtained either by adding the value for A to the extrapolated value for B at infinite dilution in A, or by adding the polarisation of the species B to that for infinite dilution of A in B. In Fig. 1 the polarisation of ether at infinite dilution in chloroform is 90·0, and the constant value assumed for the latter, being that in the pure state, is 44·9, making a total of 134·9 ; by taking the polarisation of ether as constant at 54·7, that of chloroform extrapolated to infinite dilution is 78·5, the total being 133·2. The polarisation of the ether–chloroform complex may thus be assumed to be about 134 c.c. at 20°. Provided the dielectric constants of the two components are similar, as is the case with ether and chloroform, the two values for the polarisation of the complex, calculated in this way, have been found to be close ; when the dielectric constants are different, however, the results differ in the manner to be expected.

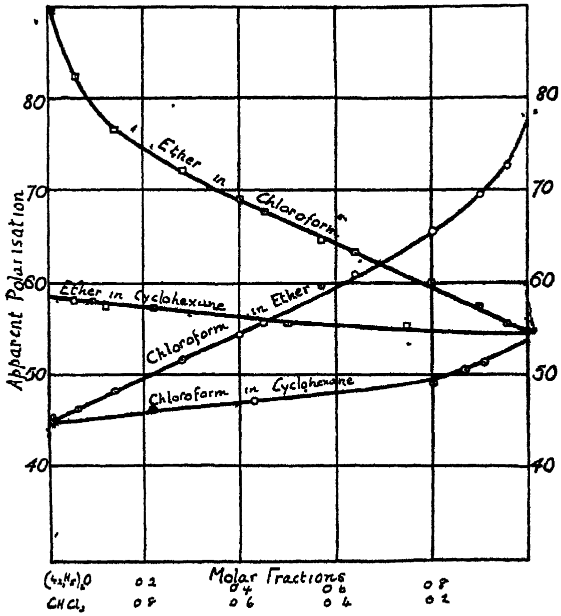

FIG. 1.

In order to obtain some indication of the extent of compound formation in the various cases, an approximate mass-action constant for the equilibrium A + B ⇋ AB, with activities expressed as molar fractions, was evaluated for most of the systems studied. The amount of complex was determined from the total polarisation and a knowledge of the polarisations of the three constituents A, B and AB, assuming the total polarisation to be an additive function of the polarisations of the separate constituents of the mixture. In applying the calculation it is necessary to use values for the individual polarisations appropriate to a medium of the same dielectric constant as that of which the total polarisation was measured: this was done by suitable interpolation or extrapolation, the polarisations being plotted for the purpose against the function of the dielectric constant $[(\epsilon - 1)/(\epsilon + 2)]^2$.

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[5] For experimental details, see Earp and Glasstone, *J. Chem. Soc.*, 1935, 1709.

In general, the mass-action "constant" remained remarkably constant over the whole range of concentration, especially when the extreme dielectric constants were not greatly different. With some systems, however, *e.g.* acetone and chloroform, in the region wherein the dielectric constant was changing rapidly with varying concentration, the mass-action expression was not altogether constant, but the results were sufficiently clear for an approximate mass-action constant to be deduced. Some of the results obtained are summarised in Table I.: the calculations are based in every case on the assumption that the complex consists of equimolecular amounts of the two constituents. Alternative calculations were made in certain cases, *e.g.* for one molecule of acetone to two of chloroform, and for three molecules of quinoline to one of chloroform, but the mass-action function showed very marked drifts, *e.g.* in the latter case from 13,000 to 0·06. The first column in the table gives the components, the next shows the molar fraction of complex present in an equimolecular mixture of the two components, then follows the corresponding mass-action constant, and in the last column is given the average value for the constant obtained from all the mixtures of a given system, the obviously divergent results being ignored.

TABLE I.—EXTENT OF COMPLEX FORMATION IN LIQUID MIXTURES AT 20° C.

System.	Molar Fraction of Complex.	Corresponding *K*.	Mean. *K*.
Diethyl ether and Chloroform . . .	0·08	0·43	0·44
„ „ „ Bromoform . . .	0·08	0·44	0·44
„ „ „ Pentachloroethane .	0·07	0·35	0·36
„ „ „ Methyl chloroform .	0·011	0·044	0·040
„ „ „ Carbon tetrachloride .	0·014	0·058	0·065
„ „ „ Carbon tetrabromide .	—	—	0·12
„ „ „ Hexachloroethane . .	—	—	0·09
Di*iso*propyl ether and Chloroform . .	0·10	0·60	0·62
„ „ „ Bromoform . .	0·09	0·49	0·49
„ „ „ Carbon tetrachloride	0·016	0·007	0·006
„ „ „ Carbon tetrabromide	—	—	0·10
ββ′-Dichloroethyl ether and Chloroform .	0·05	0·21	—
Acetone and Chloroform	0·07	0·35	—
Quinoline and Chloroform . . .	0·08	0·44	—

For a number of other systems it was not possible, for various reasons, *e.g.* limited range of liquid mixtures, variation of dielectric constant, to calculate mass-action constants, but the relative extents of compound formation, as compared with the amounts in analogous series, could be readily determined by plotting the apparent polarisation of one of the components, *e.g.* acetone, against the dielectric constant function $[(\epsilon - 1)/(\epsilon + 2)]^2$. The greater the proportion of compound the greater the deviation from the corresponding curve in a mixture with a non-polar substance, such as *cyclo*hexane. The complete results, representing the extent of complex formation, may be summarised in the following manner:

Diethyl ether

Chloroform = Bromoform > Iodoform

Chloroform ≫ Methyl chloroform

Chloroform ≫ Carbon tetrachloride < Carbon tetrabromide.

Diisopropyl ether

Chloroform > Bromoform

Carbon tetrachloride < Carbon tetrabromide.

Chloroform

Di*iso*propyl > Diethyl > $\beta\beta'$-Dichloroethyl ether.

Acetone

Chloroform > Bromoform > Iodoform.

Quinoline

Chloroform > Bromoform > Iodoform.

Discussion.

In reviewing the results the important fact becomes evident that the structure of a complex in the liquid phase may have no relationship to that of the solid compound formed by the same two components. For example, although the definite compound $CHI_3 . 3C_9H_7N$ readily separates from solutions of iodoform in quinoline, the evidence of dielectric polarisation indicates that the amount of complex formed in solution is very small. This is supported by the fact that iodoform is only sparingly soluble in quinoline. Further, it is important to note that although chloroform and bromoform do apparently form complexes in quinoline solution the amounts of the two constituents are probably in the molecular ratio of 1 to 1, and not 1 to 3 as in the solid iodoform compound. Acetone and chloroform also form the crystalline compound [6] $(CH_3)_2CO . 2CHCl_3$, but in the liquid phase the main complex formed apparently contains equimolecular amounts of the two substances. It is of interest to record another example of a similar type, although in a very different field, showing the marked difference which may exist between the nature of the solid phase and that of the liquid from which it separates. Aqueous solutions of lead halides in alkali halides definitely contain complex ions, but X-ray examination of the compounds $NH_4Pb_2Br_5$, $RbPb_2Br_5$ and $CsPb_2Cl_5$ has shown them to consist in the crystalline state of covalent molecules of lead halide packed in a lattice of alkali metal, or ammonium, and halogen ions, there being no evidence of the presence of complex ions in the crystals.[7] It is not always safe, therefore, to draw conclusions concerning the structure of a complex in the liquid phase from that of the solid, for in the latter the stoicheiometric ratio and arrangement of the constituents may be determined by considerations of atomic or ionic size and of the constants of the space lattice. In certain instances, however, where there is a marked change in colour on mixing two substances, as for example with poly-nitro-compounds and bases, and when the solid and the liquid have the same intense colour, it is probable that there is some relationship between the complexes in the two phases.[8] It may be noted in this connection that the solid iodoform–quinoline compound is much lighter in colour than is iodoform itself.

[6] Wyatt, *Trans. Faraday Soc.*, 1929, **25**, 49.

[7] Private communication from H. M. Powell and H. S. Tasker.

[8] *Cf.* Bennett and Willis, *J. Chem. Soc.*, 1929, 256 ; Moore, Shepherd and Goodall, *ibid.*, 1931, 1447.

The next matter of importance is the conclusion that in the complexes formed between ether and chloroform, or related compounds, it is the hydrogen atom or the C—H linkage of the CHX_3 molecule which is the essential factor. This is evident from the extent of compound formation with methyl chloroform or carbon tetrachloride being very much less than with chloroform itself, although pentachloroethane forms a complex in ether solution to much the same extent. According to the point of view that the complexes contain a definite chemical bond which holds the parts together, this bond may be supposed to form by the donation of one of the "lone pairs" of electrons of the oxygen atom to the hydrogen, thus $R_2O \rightarrow H . CX_3$. According to modern views on co-ordinated hydrogen the actual state would be due to resonance between the alternative structures(R_2O H—CX_3) and ($R_2\overset{+}{O}$—H $\overset{-}{C}X_3$). The variation in the extent of compound formation with changes in the nature of R_2O and of CHX_3 can be readily explained on the basis of this formulation: the presence of electron-attracting groups, *e.g.* Cl in $\beta\beta'$-dichloroethyl ether, would reduce the tendency for oxygen to donate a pair of electrons, whereas electron-repelling groups, e.g. CH_3 in di*iso*propyl ether, would increase the donating power and so there would be an increase in the extent of complex formation. Increasing the negativity of the radical X should also increase the amount of complex; this is in harmony with the results in the series iodoform, bromoform, chloroform. The observations with the acetone–CHX_3 and the quinoline–CHX_3 systems indicate that in these cases the complexes may be formulated in an analogous manner to that proposed for ethers, the oxygen and nitrogen atoms, respectively, acting as donors to form the "resonance" bond with hydrogen.

With the tetrahalogenomethanes a tendency to form complexes is definitely indicated by the polarisation measurements, but the extent is much less than with the trihalogeno-compounds. If it is assumed that the complexes involve a new covalent bond resulting from the donation of a pair of electrons from the oxygen atom of an ether or acetone, or from the nitrogen atom of quinoline, the compounds may be formulated, *e.g.* for ether, as $R_2O \rightarrow X . CX_3$. Such a formula makes the halogen bicovalent and requires it to have a valency group of ten electrons; a similar condition is supposed to apply in the polyhalides and in other compounds.[9] The tendency to form polyhalides increases in the order $Cl < Br < I$, which is the same, at least as far as chlorine and bromine are concerned, as that for the carbon tetrahalides to form compounds with ethers. The fact that hydrgen co-ordinates with oxygen much more readily than a halogen atom will increase its valency group accounts for the fact that complex formation with an ether or acetone is much more marked with the tri- than with the tetra-halogenomethanes.

It is now desirable to see how far the results recorded above can be accounted for by assuming dipole association (which must clearly be of the "head-on" type because of the increase in dielectric polarisation), instead of chemical combination, to be responsible for the formation of the complexes. The general nature of the polarisation results harmonises with this assumption, and in fact Müller[10] suggested the existence of loose complexes to account for the abnormal polarisation of acetone in carbon tetrachloride solution. Moelwyn-Hughes and Sherman[11] have also shown that the heats of formation of the ether–chloroform and acetone–chloroform complexes are of the order to be expected from a head-on union of dipoles, formulated, *e.g.* for acetone, as $[R_2\overset{+\!\!\rightarrow}{C{=}O}\ \overset{+\!\!\rightarrow}{H - C}X_3]$. The decreased extent of compound formation in passing from chloroform and bromoform to iodoform might be explained by the corresponding decrease in the moment of the C—halogen linkage and the consequent decrease in the polarisability of the C—H bond. With the tetrahalogenomethanes, on the other hand, the greater polarisability of the C—Br link than that of the C—Cl bond could be invoked to account for the greater amount of complex formation with the former. These suggestions are not inherently improbable, but they do not appear to account in a simple manner for the much greater tendency shown by the trihalogeno-compounds to form complexes than is the case with the tetrahalogenomethanes. Further, since the moment of the C = O group in a ketone is larger than that of C—O in an ether, a greater amount of compound formation might be expected with acetone than with ether: actually the proportion of complex is approximately the same in the two cases (Table I.). It does not appear a simple matter, on the basis of the concept of dipole association, to account for the order of complex formation with the three ethers studied, for it bears no relationship to the dipole moments of these substances. Unfortunately nothing is known of the moment of the C—O link in these substances. It may be noted that the results of Müller[10] indicate a greater extent of complex formation between carbon tetrachloride and acetone than between the tetrachloride and benzophenone, whereas the dipole moment of the latter ketone is actually greater than that of the former. This result is to be anticipated if electron donation from oxygen is involved, because of the electron attracting (negative) tendency of the phenyl groups.

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[9] Sidgwick, *Electronic Theory of Valency*, 1927, p. 293.

[10] F. H. Müller, *Physikal. Z.*, 1933, **34**, 688.

[11] Moelwyn-Hughes and Sherman, *J. Chem. Soc.*, 1936, 101.

If the formation of complexes is to be attributed to simple dipole association of the head-on type it is clearly pertinent to enquire why the phenomenon should be observed with ethers and ketones, and probably with other oxygen-containing compounds, *e.g.* methyl alcohol,[12] dioxan,[13] and with quinoline. Other substances do not appear to show abnormal polarisation in carbon tetrachloride and normal dipole moments are generally obtained in chloroform solution, after making due allowance for the dielectric constant of this substance, in spite of its polar nature. The view that the complex contains a chemical linkage attributes its formation to the lone pairs of electrons possessed by nitrogen and by oxygen, and these are known to be donated quite readily to other atoms. It is true that halogen atoms have lone pairs of electrons also, but they are not donated at all easily; for example, fluorine is the only halogen definitely to form a co-ordinate link with hydrogen.

It is possible that, if considered from the right point of view, there is no fundamental difference between the idea of end-on dipole association and that of compound formation involving a co-ordinate link in the cases considered. The magnitude of the carbon–oxygen link moment is undoubtedly determined by the presence of the two lone pairs of electrons on the oxygen atom and these when approaching the CHX_3 molecule may be regarded as polarising the C—H bond by tending to repel the pair of electrons involved. The result may then be represented by

$$R_2O : H : CX_3$$

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[12] F. H. Müller and Mortier, *Physikal. Z.*, 1935, 36, 371.

[13] Earp and Glasstone, *J. Chem. Soc.*, 1935, 1720.

I. A.

and it is doubtful if this is distinguishable from the resonance structure involving co-ordinated hydrogen already considered. The same argument may be extended, although not so precisely, to the compounds with tetrahalogenomethanes. It may be pointed out that a "partial bond" of the type implied would account for the low heat of formation, about 7000 cals., of the chloroform complexes,[14] and for the small dipole moment of the bond, *viz.*, about 0·5 *D* or less. The heats of formation of the complexes between amines and phenolic compounds in the liquid phase,[15] and the heats of "association" of alcohols,[16] suggest that in both instances bonds are present which are similar to those responsible for the ether–chloroform complexes.

The University,
Sheffield, 10.

GENERAL DISCUSSION.

Professor J. Errera (*Brussels*) said: The hypothesis of the formation of complexes could, as Dr. Glasstone admits, be controlled "microscopically" by studying the near-infra-red absorption of his solutions. If two molecules form a complex with "a definite chemical bond" the spectrum of this complex must differ from the spectrum of the isolated molecules.

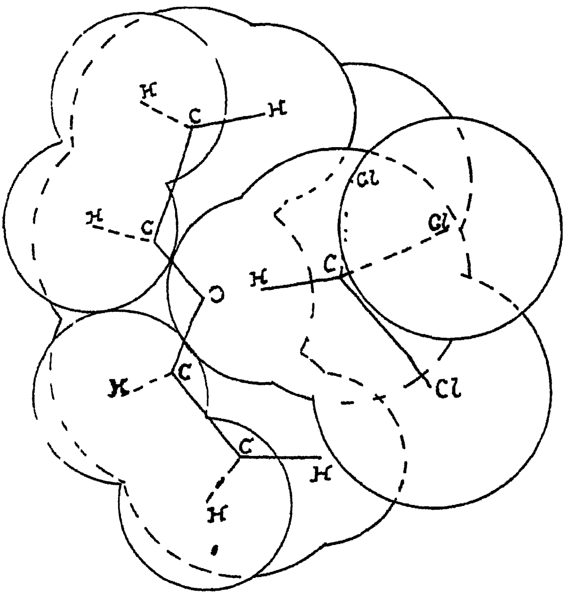

Fig. 1.

Dr. M. Magat (*Paris*) said: At this stage I emphasise the remark made above [17] on the communication of Professor Hildebrand.

(1) When we say that chloroform enters into ether as a key in a keyhole,[18] we do not mean that the chloroform takes its place between the carbon atoms of the ether; the relative positions we assume to be as in Fig. 1, reproducing a space model; *i.e.*, the carbon of the chloroform comes below the plane of C—O—C of the ether. In the bisection plane of C—O—C there are situated the O of the ether, and the H and C of the

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[14] Macleod and Wilson, *Trans. Faraday Soc.*, 1935, **31**, 596.

[15] Glass and Madgin, *J. Chem. Soc.*, 1934, 260, 1292.

[16] von Elbe, *J. Chem. Physics*, 1934, **2**, 73; Wolf *et al.*, *Z. physikal. Chem. B.*, 1935, 260, **28**, 1.

[17] *This vol.*, p. 156.

[18] M. Magat, *Z. physik. Chemie, A*, 1932, **162**, 432, particularly p. 435; *Z. Elektrochemie*, 1932, **38**, 619.

chloroform, H being as near to O as possible.[19] The polarisation measurements of Dr. Glasstone do not contradict this hypothesis.

(2) We evaluated roughly some years ago the association energy of such a complex: taking into consideration only the dipole interaction we found about 2k cal., a value too small having regard to modern experimental data. The calculation must, however, be made by assuming a reasonable charge distribution, just as has been done by Bernal and Fowler,[20] and by ourselves[21] for water, when undoubtedly the figure so calculated will be much higher. Again, we must add the London forces, which will probably explain many detail features.

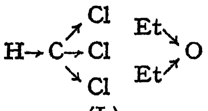
(3) Such an association, as is assumed by Dr. Glasstone must strongly change the Raman spectra of the components and, as is pointed out by Professor Henri, the ultraviolet absorption bands. Now Dadieu and Kohlrausch[22] found the Raman spectra of the mixture to be exactly the sum of those of the components ($CHCl_3$ and $(C_2(H_5)_2O)$. No new line could be observed. On the other hand, Scheibe[23] observed no anomaly in the ultraviolet C = O band in mixtures of acetone and chloroform.

So we do not see any necessity to admit a new kind of valency in this case, as Mr. Glasstone does it.

In conclusion, so far as I can remember, Professor Polanyi some years ago calculated the probability of the " tunnel " displacement of the hydrogen atoms as it is now assumed to be. Perhaps he would be so kind to tell us if it is theoretically possible.

The distance being of the order of 1Å. in our case, it is therefore not theoretically impossible for such a kind of valency to exist, although we can say that, because of the very strong C—H bond, it is not very likely.

Dr. R. J. W. Le Fèvre (*London*) said: An alternative suggestion, which would relegate the C—H bond to a subsidiary part in the process, is that the association between ether and chloroform, acetone and chloroform, etc., occurs chiefly because of electrostatic attractive forces between permanent dipoles in one molecule and the induced dipoles to which these give rise in the polarisable parts of the second. If this be so, then an important factor determining the mutual orientation of the two molecules will be the tendency of the strongest permanent dipoles of either molecule to make the closest approach to the most polarisable parts of the other. Thus, between ether and chloroform an arrangement such as (I.) will occur (since $\mu_{C—Cl} = 1{\cdot}7$, $\mu_{C—O} = 0{\cdot}9$, and the polarisability of Et compared with oxygen = 5 : 1); in this the molecular resultants are in the same sense, corresponding to a larger moment for the complex than for either individual separately.



(I.)

This is in agreement with the observation of Dr. Glasstone that such mixtures display abnormally high polarisations. Further the, slight changes caused by substitution of ether by acetone, the greater association found with dipropyl ether, the decrease in extent of association in passing from $CHCl_3$ to CHI_3, and the results recorded for carbon tetrachloride, are all predicted qualitatively by the present explanation.

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[19] For outer atomic radii see M. Magat, *Z. physik. Chemie, B*, 1932, **16**, 1; H. A. Stuart, *Molekularstruktur*.

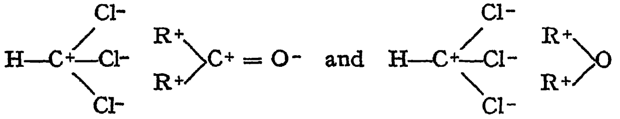
[20] Bernal and Fowler, *J. Chem. Physics*, 1933, **1**, 515.

[21] M. Magat, *Ann. Physique*, 1936.

[22] A. Dadieu and K. W. F. Kohlrausch, *Physikal. Z.*, 1930, **31**, 514.

[23] Scheibe, *Ber.*, 1926, **59**, 2617.

Dr. A. R. Martin (*London*) said : The primary thing about the chloroform molecule is the three C—Cl dipoles ; the induced dipole in the C—H bond is probably a secondary feature. The association of chloroform with acetone and ether may therefore follow the scheme :—



in which the attraction is mainly due to the action of the three negative chlorines on the polarisable alkyl groups. If this were so the extent of association with acetone and with ether would be expected to be about the same, as in fact it is.

Mr. J. D. Bernal (*Cambridge*) said : In the case of alcohol chloroform mixtures I think it is for theoretical reasons most unlikely that any form of hydrogen binding occurs between the oxygen of the ether and the carbon in chloroform. There is no reason to suppose that the hydrogen is in this case very much more loosely bound to carbon than is generally the case. It would, however, be more useful not to have to rely on theoretical arguments, but to settle the case by experiment which in this case would be relatively easy. A simple examination of the Raman spectra of ether chloroform mixtures would show by the absence of the CH vibration or a notable change of wave-length whether this hydrogen atom was concerned in binding the atoms together. In this case, I am much more inclined to think that general dipole and steric are responsible for the whole effect.

Dr. E. B. Ludlam (*Edinburgh*) said : As we have present with us both Professor Henri and Professor Errera, I should like to ask whether there has been any successful correlation, such as would be expected, of the results obtained from the examination of the absorption spectra of liquids in the ultra-violet and the infra-red, respectively, and with Raman spectra.

Professor Henri and **Professor Errera** answered that not much work had been done on the subject.

Dr. C. F. Goodeve (*London*) said : Professor Henri's suggestion that the heat of interaction between a solute molecule and the solvent could be determined from a shift in the absorption spectrum of the solute towards the *red*, is not borne out by experience. With most solutions the shift, if any, is towards the shorter wave-lengths.[24] The absorption band of hydrogen bromide in the liquid state is displaced towards the far U.V. by 2000 wave-numbers, from the position of the band for the gas.[25] There may be some connection between this displacement and the latent heat of evaporation.

Professor H. Hellmann (*Moscow*) (*communicated*) : Although after the formulation of the electrostatic theory of interaction in liquids it at first appeared that the older chemical structural conceptions of valence activity were unnecessary in this region, many new investigations show* that, in addition to electrostatic interactions more or less definite chemical valence interactions are always in force. Unfortunately, a suitable method capable of quantitative treatment of these forces is completely lacking. I believe that Pauling's method of the resonance of valence structures, applied by Glasstone, which leads to a qualitative understanding of these forces is very fruitful, not only here, but also in the whole problem of the interaction in liquids. I would like to indicate, in regard to the simplest example of the solvation of a positive ion, how it can also be made quantitatively useful.

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[24] See, for example, O. J. Walker, *Trans. Faraday Soc.*, 1935, 31, 1432.

[25] A. W. C. Taylor, *Thesis*, University of London, 1935.

* See for example the reports given here concerning the salting out effect (Albright and Williams), dipole solvation (Banks) and liquid mixtures (Glasstone).

If one forms the water molecule from a rare gas like ion and two protons then, as is known, in the completed molecule the participation of a homopolar valence structure sets in alongside the pure heteropolar valence structure, in such a way that an electron pair of the original atomic function goes over to a two-centre function and thus forms a homopolar valence bond. The heteropolar and homopolar valence structures are always in resonance with one another and through the participation of both the energy always sinks to a lower value than if only one of them were present. If a third proton is added then, naturally, the third pair of six *p*-electrons will also partially make use of the potential trough of the third proton. If now the proton is symmetrically surrounded by many water molecules, a new resonance degeneracy is brought about so that the homopolar valence can be manifested either between the first, second or third, etc., of the surrounding molecules.

By replacing the proton with any other positive ion, the entire consideration remains qualitatively valid, for we again have, in addition to the electrostatic interaction, a resonance energy of the homopolar valence structures; in other words, an electron may be transferred from each of the surrounding atoms to the ion and in this way form a valence bond with it. So long as this resonance energy is small it is indeed possible to derive a quantum-mechanical rule, *viz.*, it is equal to the quotient of the square of the transition probability between the two valence structures divided by the energy difference between each of the pure valence structures. For the case of solvation the square of the transition probability between the two valence structures is approximately equal to the sum of the squares of the transition probabilities of all the surrounding electrons to the central ion.

From this one appreciates without further calculation the fact that the heat of hydration of Ag^+ is significantly greater than that of K^+ and Na^+, although the ionic radius of Ag^+ lies between the two. On account of the greater electron affinity of Ag^+ the transition effect here plays an appreciable rôle. An estimation by means of a combined approximation procedure, which I have applied with success to other problems),[26] yielded, in fact, for the resonance energy the order of magnitude of the difference of energy between the heats of hydration of Ag^+ and K^+.

The transition probability manifests all the specific chemical properties which can never be expressed through the ionic radius and charge alone. I believe, therefore, that those remarks should be of interest in connection with the questions discussed by Dr. Glasstone and the other above mentioned authors. There is shown here a feasible way, which I hope later will be applied to the more complicated problems under discussion.

Professor J. H. Hildebrand (*Berkeley, Cal.*) said : This work seems to me to be an excellent example of impartial consideration of the several factors that may be involved. It is not easy to distinguish mere dipole interaction from chemical bond formation, since either may yield approximately satisfactory energy relations. The only certain method appears to be spectroscopic, through Roman lines or infra-red absorption, which should be investigated in connection with such studies.

It is noteworthy that ether, which does not appear to form dipole complexes with itself—its polarisation is unchanged on dilution with hexane—must exert too small a polarising effect on carbon tetrachloride to account for the observed interaction.

Although I have deliberately confined my attention largely to nonpolar molecules, I wish to point out that the vast majority of molecular species are polar, and that vigorous attacks on systems such as Dr. Glasstone has studied are essential to useful and comprehensive solubility theory.

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[26] Hellmann, *J. Chem. Physics*, 1935, **3**, 61; *Acta Physicoch. U.R.S.S.*, 1935, **1**, 913; Hellmann and Kassatotschkin, *J. Chem. Physics.*, 1936, **4**, 324; *Acta Physicoch. U.R.S.S.*, 1936, **5**, 23.

It may be worth while to summarise what appear to me to be the factors to be considered in endeavouring to treat such systems. They are, dipole moment, but including the geometry of the molecules; the London forces, their strength and location; and the chemical bonds that may be formed.

In reference to this last, it is interesting to note that the hydrogen bond Dr. Glasstone proposes, in which one link is to carbon, is something rather new, for the atoms heretofore recognised as linked in this way have been fluorine, oxygen and nitrogen. It will be interesting if carbon can be added to this list.

Dr. R. J. W. Le Fèvre (*London*): The classification of substances into "polar" and "non-polar" may tend to obscure the truth. The *resultant* polarity of a molecule may be irrelevant in the present connection. For example, several polynitro-aromatic hydrocarbons are non-polar and yet associate strongly with many substances, notably with their parent and other aromatic hydrocarbons. If the *individual* polar links are considered, however, a mechanism for such cases is obvious: the molecules —being flat sheets—lie together very much as the carbon layers in graphite, the strong $C \rightarrow NO_2$ dipoles of the nitro-compounds inducing corresponding moments in the hydrocarbons. Stability is given to the unions by the electrostatic attractions between the induced and permanent moments (the process is the electrical analogy between the attraction of a sheet of iron by a rigidly fixed system of magnets); this interaction energy can be estimated in simple cases and appears to be sufficient to explain the known results. A similar formulation is obvious for the numerous picrates and styphnates encountered in organic chemistry.

Mr. J. D. Bernal (*Cambridge*) said: It might be useful in this stage of the discussion to draw certain distinctions between the geometrical types of association which may be expected to occur in liquids and liquid mixtures. I find it convenient to introduce for liquids the terms which I used for crystals at a previous discussion in the Faraday Society. In any association we may treat the forces between the units as being either of approximately the same strength or of very different strength. The first type I have chosen to call homodesmic, the second heterodesmic (after desmos— a bond). In the first homodesmic case we call those liquids associated for which there is some type of bonding other than the universally present London forces which bind all molecules together. In the other case, such extra bonds are present only between pairs or small groups of molecules which in turn are held together by London forces alone. This is a characteristically heterodesmic arrangement of a liquid which may truly be called associated. The extra forces which exist in homodesmic compounds, on the other hand, are for practical purposes either ionic in the fused salts, homopolar in the fused sulphides, etc., and hydrogen or hydroxyl bonds in acid or neutral organic liquids. Of these, only the properties of the last two have been effectively studied. The typical substance here is water. As Fowler and I have shown, and as has been amply confirmed by subsequent studies there is no assemblage of groups of molecules, but rather the whole of the liquid is a network of molecules held together by hydroxyl bonds. It is primarily the fact that in water the molecules are held together by bonds with definite directions to four (and no more) other molecules that this liquid has the peculiar properties which has made it the type of associated liquid. Similar association due to hydroxyl bonds is found only in the polyhydric alcohols or corresponding amino compounds and very weak acids.

In all cases, however, where the molecule possesses only one effective hydroxyl group or only a few, if it is a very large molecule, we get the tendency of the hydroxyl groups to be held together by hydroxyl bonds and, consequently, to be shielded from interacting further with one another; thus the liquid will be composed effectively of normal London molecules of sizes, twice, or a small number of times that of the single molecule. This is the case for the monohydric alcohols and acids. The stronger the hydroxyl bond the more complete the isolation of the molecule pair and the more the substance will resemble a normal liquid, thus deuteroacetic acid has a higher and not a lower vapour pressure than normal acetic acid.

The other case of the type of complex formation mentioned by Glasstone as exemplified by the chloroform quinoline complex, is due to quite special circumstances, namely, the fact that certain molecules are of such a shape that when fitting together in a crystal structure they leave gaps which can be filled by other generally smaller molecules. Some particular configuration gives an exact fit and in that case a molecular compound of particular stability is formed. There is no evidence from the formation of such compounds of any particular molecular forces. Still less should one expect any special association forces in the liquid. I have, myself, for instance been studying the complex of the molecular compounds of $CHI_3\ 3S_8$ and $SbI_3\ 3S_8$ which are in the crystal state isomorphous. In this case there could be no question of hydrogen bond formation in the liquid since the latter compound does not possess a hydrogen atom.

It may also be useful to make quite clear at this stage what I mean by hydrogen and hydroxyl bond, though this has been already stated in a published paper.[27] The distinction is, in some sense, a quantitative one, though, in the great majority of cases the bond could definitely be stated to be of one kind rather than the other. In the hydrogen bond a proton is situated in such a way that it is impossible to say to which of two atoms it is most closely attached. It may be considered as attached most of the time to one or other of two adjacent atoms—usually oxygen—but to move at some fairly high frequency from one position to the other. In the hydrogen bond the proton is consequently held very loosely, and is able to attach the two other atoms to one another with the maximum force. It leads to an interatomic distance between them if they are oxygens of from 2·5 to 2·65A, and it has an energy of about 8Kc. The looseness of the hydrogen binding means that effectively its vibration frequency cannot be detected even in infra-red or Raman spectra. Thus in acetic acid and deuteroacetic acid no change in infra-red or Raman spectrum is observed, showing that the acid hydrogen atom does not contribute to the spectra.

In the hydroxyl bond, on the other hand, there is generally one proton in each of two neighbouring atoms, usually oxygen atoms, the protons consequently are not so detached from the other atoms as in the hydrogen bond, and are less effective in holding these together. The usual distance is between 2·7 to 2·9A, and the energy about 5Kc. Here the proton vibrations are detectable, both in Raman and infra-red spectra, but, owing to the presence of a neighbouring atom the normal OH frequencies are lowered, usually from 3600 for free OH to 3200 for OH in the hydroxyl bond. This has been beautifully shown by the results Professor Errera has communicated to this meeting. No doubt intermediate types exist, but it would be fairly safe to call anything a hydroxyl bond which showed a O—O distance of 2·55A and no characteristic Raman spectrum and a hydroxyl bond one which showed an OO distance of 2·75 and a Raman frequency of 200.

Finally, I should like to say a few words on the methods now available for treating intermolecular forces in liquids. In my opinion the time is now past when we were restricted to considering a molecule as a sphere of uncertain dimensions possessing only a loose dipole and Van der Waals' attraction and a measurable dipole moment. We know enough both of the shapes of molecules and the nature of the forces between them to go at any rate in many cases far beyond this. The most important characteristic is whether the molecule possesses, not so much a dipole moment, but a highly divergent electrical field, *i.e.*, where its attraction is not spread largely over its surface, but is concentrated at one or two points. Where this is not the case we may enquire whether the shape of the molecule is such that free rotation may be expected to take place in the liquid. This will be so not only for all liquids in which such rotation is known to take place in the crystalline phase but for many others, because in a liquid the irregularity of configuration means effectively that the potential field in respect to rotary movements is much more even than in the case of a crystal and is also, owing to the increase in volume, much weaker. It should be possible in most cases to determine whether such free rotation takes place, by the study of Raman spectra of the liquid. All liquids in which free rotation takes place can be reasonable strictly treated as liquids with spherical molecules and the many remarkable uniformities observed in liquids and commented on in the present discussion are probably due to this cause. For liquids whose molecules are so aspherical in shape that free rotation cannot take place theoretical treatment is obviously more difficult though some help could probably be got from the study of the libration frequencies given by the wings of the Raman spectrium.

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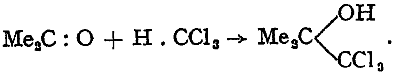
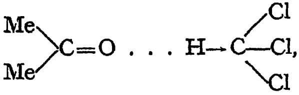
[27] Bernal and Megaw, *Proc. Roy. Soc.*, *A*, 1935, **151**, 384.

For liquids whose molecules have definite points of attachment it is also possible to provide the beginning of a theory. In the simplest case, that of water, Magat has beautifully shown that, beginning with the model which Fowler and I worked out, it is possible to go further than the calculation of the potential energy of interaction between such molecules and to calculate the libration frequencies of these molecules with respect to one another. In this way he has explained the whole of the intermolecular Raman spectra of ordinary and heavy water, and this result has been confirmed by Cartwright in studies of the extreme infra-red absorption. In dealing with such liquids it should be possible, from a knowledge based on crystal analysis and spectroscopy, to set up precise models of the molecules, to put these models together and to calculate the positions of minimum energy of the principal vibrations. The conclusions drawn from such a study will be fairly applicable to the liquid as a whole because in these cases also the molecular forces are extremely short range and what holds for a pair of molecules will only be slightly distorted when applied to the whole liquid. It is true that so far little progress has been made along these lines, but I feel this is largely due to the fact that chemists have not yet realised the full power that the new methods of molecular physics have put into their hands.

Professor J. H. Hildebrand (*Berkeley, Cal.*) said: I wish to express the opinion that the summary just given by Mr. Bernal is at least as important as any contribution yet made to this symposium. I hope it will be published in full.

Professor J. Kendall (*Edinburgh*) said: It is true, as Dr. Bernal has noted, that a great deal of confusion has resulted through the attempt to treat all cases of association between the two components of a solution on the same basis. Fifteen years ago[38] I called attention to the fundamental distinction between *addition compounds*, formed by the direct union of solvent and solute molecules, and *substitution compounds*, formed by the replacement of part of an associated solvent molecule by the solute. The controlling influence in the first type is *dissimilarity* in the electrochemical character of the constituent groups; the controlling influence in the second type is *similarity* (*e.g.*, in phenol-cresol mixtures). Addition compounds are "heterodesmic"; substitution compounds are "homodesmic." It is immaterial which nomenclature we adopt; the essential point is that no single theory can embrace the two types.

Dr. R. J. W. Le Fèvre (*London*) said: If a mixture of chloroform and acetone is treated with alkali a solid, known as "chloreton" is produced. This substance definitely contains a hydroxyl group; during its formation, therefore, it might appear that the relative orientations of the molecules must have been such that addition of chloroform across the ketonic link could occur:  $Me_2C:O + H.CCl_3 \rightarrow Me_2C\begin{matrix} OH \\ CCl_3 \end{matrix}$. The formulation used by Dr. Glasstone, *viz.*,  $\begin{matrix} Me \\ Me \end{matrix}\!>\!C{=}O \ldots H{\rightarrow}C\begin{matrix} Cl \\ Cl \\ Cl \end{matrix}$, thus attributes to the association complexes in the liquid mixture a structure which would appear to favour the initiation of this reaction. However, the absence of definite knowledge concerning the mechanism of the action of the catalyst reduces the value of such evidence.

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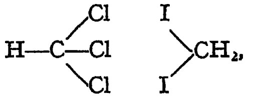
[38] *J. Amer. Chem. Soc.*, 1921, 43, 1853.

Dr. S. Glasstone (*Sheffield*), in reply, said: The possibility of confirming the presence of a new chemical bond in a complex such as that formed between ether and chloroform by means of infra-red or Raman spectra may not be as simple as appears at first sight. There is, on the one hand, the point indicated by Bernal, in his contribution, that a hydrogen bond may not yield a vibrational spectrum and, on the other hand, the possibility that dipole or steric association of two molecules may result in such perturbations as to produce changes in the vibrational bands corresponding to the various linkages, even if there is no new chemical bond in the complex. It must also be remembered that at ordinary temperatures, even in the most favourable case, a mixture of chloroform and ether contains less than 0·1 molar fraction of complex; hence the infra-red, Raman or ultra-violet spectra of the simple molecules will be almost as intense as in the pure components, whereas any spectrum due to the complex will be relatively feeble.

The steric effect to which Magat has called attention may well be one of the contributory factors in complex formation, but it is probable that other influences are operative. The apparent lock and key arrangement as depicted in the diagram on page 206 does not take into account the possibility of free rotation about the O—C bond of ether, and in any case it does not seem possible to devise such a compact structure for the complex formed between acetone and chloroform. An almost spherical molecule of the type indicated should have a relatively high vapour pressure, although in actual fact it has a very low volatility. According to the steric point of view, the decreasing tendency for ether to form complexes in the series chloroform, bromoform, iodoform, would presumably be attributed to the increasing size of the halogen atom: if so, a test might be provided by a study of complex formation between ether and trinitromethane or triphenylmethane derivatives. If a hydrogen bond is responsible for complex formation the presence of highly negative groups attached to the carbon atom should favour the production of complex, but the steric theory would imply only a small tendency in this direction. Further, if spatial considerations are pre-eminent there seems to be no reason to suppose that trimethylmethane will not form a complex with ether: according to the chemical point of view, however, this should certainly not occur. It may be pointed out that as drawn in the figure on page 206, the distance between the centres of the carbon and oxygen atoms of chloroform and ether respectively, is about 2Å., and it is doubtful whether anything like such close proximity would be possible unless the hydrogen atom played some part in linking the oxygen and carbon atoms. As Professor Hildebrand has mentioned, the suggestion of a hydrogen bond to carbon is somewhat unusual: it should be emphasised, however, that only when there are a number of negative groups attached to the carbon atom is the electron attracting tendency sufficient to permit the hydrogen atom to take part in the formation of a resonance bond. The heat of formation of the ether–chloroform complex is about 7000 cals. per gm.

mol., a value in harmony with the suggestion that a hydrogen bond is present.

The alternative formulations proposed by Le Fèvre and by Martin are virtually identical, the formation of the ether–chloroform complex being attributed to dipole association resulting from the influence of the C—Cl dipole on the polarisable alkyl group: the C—H bond is supposed to be a secondary factor in complex formation. If this were so it would not be easy to account for the marked decrease in the extent to which the complex is obtained, *viz.*, 0·08 to 0·01 molar fraction, when the hydrogen atom in chloroform is replaced by a methyl group. The behaviour might be attributed to the influence of the latter on the C—Cl dipole, but if so it is surprising that methyl and chlorine operate in the same direction as far as the extent of complex formation is concerned. Some information as to the importance or otherwise of the C—H bond might be obtained by studying mixtures of deuterochloroform and ether: according to the view that a resonance bond is present the extent of complex formation should be appreciably greater than with ordinary chloroform. Structures of the type suggested, involving dipole association, would not explain the increase of polarisation obtained with chloroform and quinoline mixtures unless the influence of the nitrogen atom were ignored. At this point it may be emphasised that the formulations of the type under discussion do not lay sufficient stress on the need for the presence of an oxygen or nitrogen atom, or its equivalent, *e.g.*, sulphur or phosphorus, in the molecule which forms a complex with chloroform. For example, there appears to be no fundamental reason otherwise for the non-existence of complexes of the type,



since the moment of the C—Cl dipole is greater than that of C—I and the iodine atom is strongly polarisable.

It appears on the whole that there is no decisive evidence against the presence of a hydrogen bond in the ether–chloroform complexes, whereas there is a great deal in its favour. The only satisfactory method of distinguishing between the different points of view, namely of bond formation as opposed to dipole or steric association, although in certain cases, as pointed out in the paper contributed to this discussion, they may be indistinguishable, would be to examine a number of mixtures in which the theories would lead to the expectation of quite different results. Some of these have been already indicated, and others could no doubt be suggested.

Although the remarks of Dr. Le Fèvre concerning the structure of the highly coloured complexes formed by nitro-compounds and hydrocarbons are only indirectly connected with the scope of the immediate discussion, attention may be called to the fact that a careful consideration of the work of Hammick and Sixsmith [29] and of Bennett and Wain [30] shows that the situation is not simple. Some of the evidence in favour of chemical bond formation appears to be difficult to controvert.

Since the discussion was held a paper has appeared by Horiuti and Sakamoto,[31] in which it is shown that the hydrogen in chloroform is able to exchange readily with deuterium in heavy water in the presence of alkali. This result indicates that the hydrogen has some tendency to separate as a proton and its ability to form a hydrogen bond would consequently not be surprising.

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[29] *J. Chem. Soc.*, 1935, 580.
[30] *Ibid.*, 1936, 1108.
[31] *Bull. Chem. Soc. Japan*, 1936, 11, 627.

DIPOLE SOLVATION.

By W. H. Banks.

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I. Energy of Transference between Solvents.

The free energy of a molecule in a medium may be expressed by

$$(\bar{F} = {}_0\bar{F}_0 + \Delta\bar{F}_0 + RT \ln a) \quad . \quad . \quad . \quad (1)$$

where $\bar{F}$ is the partial molar free energy of the molecule existing under such conditions that its activity is a; ${}_0\bar{F}_0$ is the absolute energy in a given state; $\Delta\bar{F}_0$ is the change of free energy accompanying the transfer from this state to conditions under which its activity is unity.

For a solution, it is convenient to consider ${}_0\bar{F}_0$ as the molar energy in a vacuum. Choosing an activity scale such that at infinite dilution the activity is unity, $\Delta\bar{F}_0$ then becomes the free energy of transfer from a vacuum to the infinitely dilute solution. This is defined as the free energy of solvation.

On the basis of a very simple model for a polar molecule assuming Coulomb forces acting through a continuous dielectric right up to the boundaries of the molecule, it is possible to calculate a value for this energy of transfer. Martin[1] carries out this simple calculation by considering two charged spheres in contact surrounded by a larger sphere. By identifying the radius of this sphere with the molecular radius and using this as the lower limit of integration for the total energy in the medium, he necessarily neglects the internal field of the sphere and deduces the energy of transference to be

$$-\frac{\mu^2}{3a^3}\cdot\left(\frac{1}{D} - 1\right) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where μ is the dipole moment of the solute molecule, a is the molecular radius, and D the dielectric constant of the medium.

In a more rigid derivation, Bell[2] takes into account the field which exists inside the sphere (and which will vary from medium to medium), and assuming, quite arbitrarily, that the dielectric constant of the medium inside the sphere is unity, deduces

$$-\frac{\mu^2}{3a^3}\cdot\left(\frac{D-1}{2D+1}\right) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Kirkwood[3] has pointed out certain errors in Bell's derivation and has proposed

$$-\frac{\mu^2}{a^3}\left\{\frac{D - D_i}{2D + D_i} + \frac{D_i - 1}{D_i + 2}\right\} \quad . \quad . \quad . \quad (4)$$

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[1] Martin, *Phil. Mag.*, 1929, **8**, 550.
[2] Bell, *Trans. Faraday Soc.*, 1931, **27**, 797.
[3] Kirkwood, *J. Chem. Physics*, 1934, **2**, 351.

which would appear to be the equation open to the least objection. Assuming that the dielectric constant of the medium of the sphere D_i is unity, Kirkwood's equation becomes

$$-\frac{\mu^2}{a^3}\left(\frac{D-1}{2D+1}\right),$$

a result which is three times as large as Bell's.

It is partly the object of this paper to employ existing data to test these equations, but mainly to indicate that there are other factors which must be taken into account.

These equations express the change in energy due entirely to environmental changes and take no account of any solute solvent interaction. It is, therefore, proposed to consider the free energy of solvation as the sum of two terms: one, which may conveniently be referred to as the "environmental" solvation energy and denoted by $\Delta\bar{F}_e$, the other the "Interaction" energy denoted by $\Delta\bar{F}_s$,

so $$\Delta\bar{F}_0 = \Delta\bar{F}_e + \Delta\bar{F}_s.$$

$\Delta\bar{F}_s$ is obviously the term not taken into consideration by the simple theories.

From the considerations which are the object of this paper, it will be seen that $\Delta\bar{F}_s$ is in some cases considerable in magnitude, and in the light of these results it is easy to understand, at least in part, why only a semi-quantitative agreement with the simple electrostatic model has been found (*cf.* Bell[4]).

In this paper, data for the distribution at 25° C., of various solutes between water and solvents of varying dielectric constant, has been examined, and the comparative values of $\Delta\bar{F}_0$ calculated. It follows from equation 1 that distribution of a substance between two immiscible solvents affords an excellent means of comparing energies of solvation. The serious limitations of this method, due to mutual solubility of the solvents, must at the same time be fully realised and deductions made accordingly.

For such distribution between solvents A and B it follows that

$$\Delta_A\bar{F}_0 - \Delta_B\bar{F}_0 = RT \ln a_B/a_A \text{ or } RT \ln C_B f_B/C_A f_A,$$

where C and f refer to the concentration and activity coefficient respectively.

Treatment of Data.

Method.

The derivation of the partition coefficient at infinite dilution, from data at finite concentrations, offers difficulty because of the uncertain variation of the activity of the solute. In this work no account has been taken of the variation in activity coefficient in the water phase, except a correction for ionisation where necessary. For the variation in the other phase, it has been found satisfactory in most cases to employ "association" constants, though with no intention of ascribing any such definite significance to them, apart from being a convenient way of expressing deviation from ideal behaviour.

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[4] Bell, *J.C.S.*, 1931, 1376.

The following relationship is derived for p_0, the partition coefficient at infinite dilution (with $p_0 = {}_{\mathrm{U}}C_1/{}_{\mathrm{U}}C_2$),

$$2K\,{}_{\mathrm{U}}C_1/p_0^2 = C_2/{}_{\mathrm{U}}C_1 - 1/p_0,$$

where K is the dimeric association constant. C_2, ${}_{\mathrm{U}}C_2$, ${}_{\mathrm{U}}C_1$ represent respectively concentrations of total molecules and simple molecules in the non-aqueous phase, and undissociated molecules in the aqueous phase.

TABLE I.

Solvent.	$1/D$.	p_0.	K.	Concentration Range. Moles/litre.	$-(\Delta\bar{F}_{0\,\mathrm{H_2O}} - \Delta\bar{F}_{0\,\mathrm{sol.}})$.
Acetic Acid (at 25° C.).					
Decalin [a] . .	0·498	200 ± 80	1·16	5·0 — 11·0	3141 ± 200
Carbon tetrachloride [c]	0·450	66·6 ± 6·7	(21·3)	4·8 — 9·6	2490 ± 170
p-Xylene [a] . .	0·443	26·3 ± 3·8	2·53	1·6 — 8·0	1938 ± 74
Benzene [b] . .	0·439	37·7 ± 3·8	2·67	0·7 — 3·0	2152 ± 56
m-Xylene [a] . .	0·422	52·6 ± 4·0	12·5	0·9 — 9·0	2349 ± 48
Toluene [c] . .	0·418	40·0 ± 9·0	—	0·3 — 5·0	2186 ± 107
o-Xylene [a] . .	0·388	31·3 ± 5·0	3·66	2·0 — 9·0	2040 ± 88
Ether [b] . .	0·231	2·049 ± ·008	0·21	0·05 — 0·09	425 ± 2
Ethyl acetate [d] .	0·156	0·87 †	—		(— 81)
Amyl alcohol [b] .	0·067	1·083* ± ·009	—	0·9 — 13·0	47 ± 4
Benzaldehyde [d] .	0·056	0·44 †	—		(— 488)
Nitro benzene .	0·028	0.60 †	—		(— 305)
Monochloracetic Acid (at 25° C.).					
Carbon tetrachloride [e]	0·45	278 ± 50	67	0·03 — 1·0	3336 ± 98
Benzene [f] . .	0·439	40 ± 4	1·0	0·7 — 3·0	2187 ± 58
Toluene [e] . .	0·418	157 ± 50	495	0·1 — 1·0	2999 ± 163
Carbon disulphide [a]	0·380	575 ± 100	500	6 — 11	3767 ± 94
Bromoform [f, a] .	0·22	33 ± 5	—	2 — 9	2073 ± 84
Chloroform [e] . .	0·202	27 ± 3	8	0·1 — 0·6	1953 ± 82
Ethyl bromide [e] .	0·106	15·4 ± ·7	1·78	0·09 — 0·7	1619 ± 28
Nitro benzene [e] .	0·037	8·07 ± ·54	0·44	0·1 — 0·8	1237 ± 40
o-Nitro toluene [e] .	0·028	7·04 ± ·15	2·93	0·04 — 0·8	1157 ± 13
Ammonia (at 25° C.).					
Carbon tetrachloride [a]	0·450	238 ± 11		2·0 — 8·0	3245 ± 25
Bromoform [a] .	0·222	40 ± 2		2·0 — 8·0	2187 ± 24
Chloroform [g] . .	0·202	23·94 ± ·01		0·1 — 3·0	1882 ± 0
Amyl alcohol [b] .	0·066	7·25 ± ·25		0·8 — 6·0	1174 ± 23

[a] International Critical Tables.

[b] Hertz and Fischer, *Ber.*, 1904, 4746.

[c] Smith, *J. Physic. Chem.*, 1921, 215.

[d] Waentig and Pescheck, *Z. physik. Chem.*, 1919, **93**, 529.

[e] N. A. de Kolossowsky and F. S. Kulikow, *Z. physikal. Chem.*, 1934, **169**, 459.

[f] Smith, *J. Physic. Chem.*, 1921, 204.

[g] Davies and Matthews, *J.C.S.*, 1933, 1435.

* Hertz and Fischer's values are moderately constant over the concentration range studied. They give the mean as 0·923 ·007 at 20° C. They quote one value at 25° C. at C = 8·526, giving 0·934. This is almost within experimental error of the value at 20° C., so the values at 20° C. are used as data for 25° C.

† These values are uncertain as they refer only to a measurement at one concentration, the value of which is uncertain, since it is quoted in terms of volume of alkali required for neutralisation of the acid distributed in one phase.

Most of the available data at 25° C. has been examined critically and extrapolated to zero concentration, using the above linear relationship between $C_2/{}_UC_1$ and ${}_UC_1$. For one or two cases extrapolation is uncertain owing to marked curvature, suggestive of more complex "association," but in cases where this curvature is slight in dilute solution, the limiting slope has been used to calculate K, which is indicated in the table by being bracketed. In the case of solutions in alcohols the association plot is characterised by a negative slope. All such peculiarities are indicated in the tables. Ionisation in the aqueous phase has been corrected for by use of constants taken from the International Critical Tables, or the latest values in the literature.

The probable error of extrapolation is indicated, where possible, but these estimates refer only to probable errors in extrapolation and do not refer to the error introduced by the mutual solubility of the solvent phases.

Table I. shows in column 1, the solvent; in column 2, the reciprocal of the dielectric constant; in column 3, the extrapolation value of the partition coefficient, p_0; and in column 4, the "association" constant. Columns 5 and 6 show respectively the concentration range and energy of transfer calculated from

$$\underset{H_2O}{\Delta F_0} - \underset{sol.}{\Delta F_0} = -RT \ln p_0.$$

The latter are shown plotted against the reciprocal of the dielectric constant in Fig. 1, where the diameter of the circle enclosing each point is proportional to the estimated error. It is apparent that there is approximately an inverse relation between the free energy of transfer and the dielectric constant of the solvent, as required by equation (2). This is perhaps more conclusive in the case of ammonia and monochlor acetic acid than for acetic acid, where a considerable scattering is observed among the lower values of $1/D$. It is of course not possible

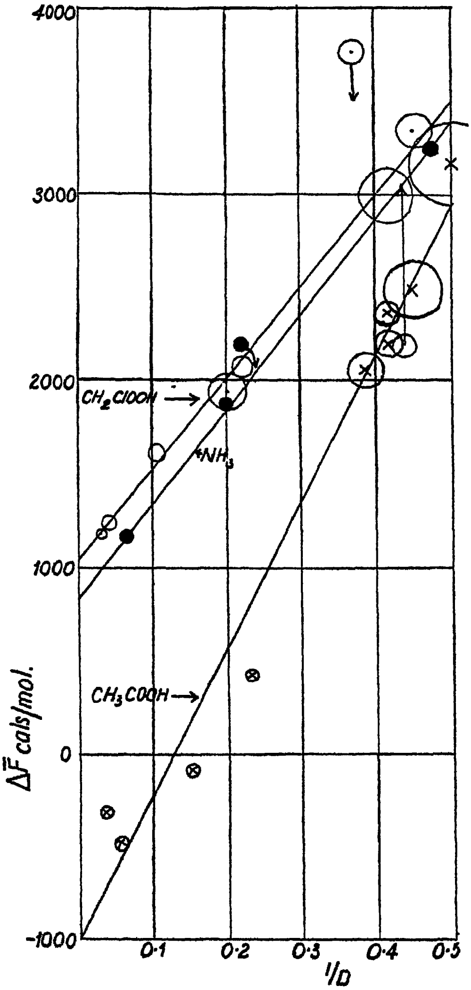

Fig. 1.—Free energy of transfer of $CH_2ClCOOH$, NH_3, CH_3COOH between water and solvents as a function of dielectric constant at 25° C.

to place any significance on this scattering, owing to the uncertain error introduced by mutual solution of the phases; although the values for distribution between water, benzaldehyde; water, ethyl acetate; and water, nitrobenzene, are uncertain for reasons given in the table. Their order of magnitude only is considered correct. There is one approximate guide, however, and that is that for values of p_0, where $p_0 > 1$, mutual solubility will tend to reduce and consequently $(\underset{H_2O}{\Delta F_0} - \underset{sol.}{\Delta F_0})$ is too small. For values of p_0, where $p_0 < 1$, mutual solubility will tend to raise these values and consequently the energy of transfer will be overestimated.

These plots are not exactly a conclusive test of the three equations. A better test of their relative applicability is afforded by calculating the value of $\mu^2/3a^3$ which should be characteristic of each solute.

Equations of Martin, Bell and Kirkwood.—Comparison 1.

Values of $\mu^2/3a^3$ calculated from the data from equations (2) and (3) are shown in Table II. The values corresponding to the solvents benzaldehyde, nitrobenzene, and ethyl acetate are not included in this test for acetic acid.

TABLE II.

Solvent.	$\left(\frac{\mu^2}{3a^3}\right)$ (Bell).	Deviation from Mean.	$\left(\frac{\mu^2}{3a^3}\right)$ (Martin).	Deviation from Mean.
Acetic Acid.				
		Mean 7759.		*Mean 4933.*
Decalin	9822	+ 2063	6043	+ 1110
Carbon tetrachloride	8630	+ 871	5369	+ 436
p-Xylene	7134	− 625	4507	− 426
Benzene	7975	+ 216	5051	+ 168
m-Xylene	8986	+ 1127	5725	+ 792
Toluene	8412	+ 653	5386	+ 453
o-Xylene	8377	+ 618	5439	+ 506
Ether	2736	− 5023	1945	− 2988
Average deviation from mean: Bell equation, 18 per cent.; Martin equation, 17 per cent.				
Monochloracetic Acid.				
		Mean 26900.		*Mean 49149.*
o-Nitro toluene	56430	+ 29530	76122	+ 26973
Nitro benzene	46164	+ 19264	40945	− 8204
Ethyl bromide	21023	− 5877	17314	− 31835
Chloroform	14158	− 12742	10311	− 38838
Toluene	11580	− 15320	73961	+ 24812
Carbon tetrachloride	12043	− 14857	76243	+ 27094
Average deviation from mean: Bell equation, 60 per cent.; Martin equation, 51 per cent.				
Ammonia.				
		Mean 12313.		*Mean 15467.*
Carbon tetrachloride	7000	− 5313	8933	− 6534
Bromoform	10440	− 1873	14582	− 885
Chloroform	10146	− 2167	14148	− 1319
Amyl alcohol	21657	+ 9344	24205	+ 8738
Average deviation from mean: Bell equation, 28 per cent.; Martin equation, 38 per cent.				

The values under $\mu^2/3a^3$ calculated from Bell's equation will apply equally well to Kirkwood's relation; furthermore, any such conclusions as to their accuracy are identical. Reference will, therefore, only be made to Bell and Martin in the table.

For ammonia and acetic acid, slightly better agreement is shown with the Bell and Kirkwood equation, giving constants having average deviations from the mean of 28 per cent., 18 per cent. respectively, against 38 per cent. and 18 per cent. deviations for the Martin equation. The reverse is true of mono-chloracetic acid, which shows a 51 per cent. and 60 per cent. deviation for the Martin and Bell equations respectively. For reasons to be considered later, this test is inconclusive. Nevertheless the conclusion reached is that the figures as they stand are in noway accurately accounted for by either equation. The simple models predict only semi-quantitatively the trend with change in dielectric constant.

Interaction Solvation Energy.

From the graphs relating transference energy and dielectric constant, it is assumed as a first approximation that, for the three solutes examined, a linear relationship holds between these quantities as given below.

monochloracetic acid $-(\underset{H_2O}{\Delta\bar{F}} - \underset{sol.}{\Delta\bar{F}}) = 1040 + 4800/D$ or
$1100 + 4800\,(1/D - 1/80)$
Acetic acid ,, ,, $= -1000 + 7800/D$ or
$-902 + 7800\,(1/D - 1/80)$
Ammonia ,, ,, $= 840 + 5000/D$ or
$903 + 5000\,(1/D - 1/80)$

where the second form of the equation is in the form of the Martin equation (using $D_{H_2O} = 80$).

It is immediately obvious that they differ from the form demanded by theory, by a term which is a characteristic constant for each solute. This is direct indication of the inadequacy of the theory, and applies equally well to the equation of Bell; since a plot of $-\Delta F$ against $\left(\frac{1}{2} - \frac{D-1}{2D+1}\right)$, although giving an approximate linear relationship, does not give $\Delta F = 0$ when this function becomes zero. Instead, it gives the same extrapolated values as the Martin equation. Such a result suggests the necessity of considering the additional energy term—" interaction " energy. The quantities 1100, -902, 903 cals./mol. are thus considered measures of this energy. The remarkable implication of this is the constancy of this energy for most of the solvents. There are two possible explanations: —

1. that the energy of interaction varies in a simple regular manner with $1/D$,
2. that water as a solvent is unique, having an interaction energy so large compared with other solvents as to mask (owing to inaccuracies in the data) any specificity due to them, except where marked deviations occur, as in the case of benzene solutions.

That the latter hypothesis is tenable follows from the fact that the energy of transfer between solvents (other than water) A and B, to take the case of mono-chloracetic acid, is given by

$$-(\underset{A}{\Delta F_0} - \underset{B}{\Delta F_0}) = 4800\,(1/D_A - 1/D_B).$$

A result which contains no constant term.

Further Test of the Equations of Martin and Bell.

It now follows that the energies of transfer, as they stand, are not directly applicable to these equations and must be corrected for the interaction energy. This is done for acetic acid, monochloracetic acid and ammonia, using the interaction energies — 902, 1100, and 903 respectively, and adopting the same procedure as with the uncorrected figures (see Table II.) The results of this test are shown in Table III. Here the Martin equation is in better agreement with the corrected figures, giving mean deviations of 16·5 per cent., 11·7 per cent. and 7 per cent., as compared with 21·3 per cent., 23·0 per cent. and 14·0 per cent. for the Bell equation. It should be remembered that these calculations are based, in the case of the Bell and Kirkwood equations, upon the rather arbitrary choice of unity for the dielectric constant of the medium of the sphere surrounding the dipole. Bell obtained evidence of slightly better agreement, employing a value of three, but there does not appear to be any theoretical basis for this.

TABLE III.

Solvent.	$\left(\frac{\mu^2}{3a^3}\right)$ (Bell).	Deviation from Mean.	$\left(\frac{\mu^2}{3a^3}\right)$ (Martin).	Deviation from Mean.
Acetic Acid.				
		Mean 10816.		*Mean 7209.*
Decalin . . .	13880	+ 3064	8539	+ 1330
m-Xylene . . .	12810	+ 1994	8181	+ 972
p-Xylene . . .	10810	— 6	6832	— 377
o-Xylene . . .	12480	+ 1664	8106	+ 897
Ether . . .	9170	— 1636	6521	— 688
Benzene . . .	11680	+ 864	7398	+ 189
Carbon tetrachloride .	12100	+ 1284	7525	+ 316
Toluene . . .	12260	+ 1444	7847	+ 638
Amyl alcohol . .	2159	— 8657	1932	— 5277

Average deviation from mean: Bell equation, 21·3 per cent.; Martin equation, 16·5 per cent.

Monochloracetic Acid.				
		Mean 6036.		*Mean 4884.*
o-Nitro toluene .	2781	— 3255	3750	— 1134
Nitro benzene .	5112	— 924	5709	+ 825
Ethyl bromide .	6741	+ 705	5551	+ 667
Chloroform .	6189	+ 152	4507	— 377
Toluene . .	7328	+ 1292	4680	— 204
Carbon tetrachloride	8065	+ 2029	5106	+ 222

Average deviation from mean: Bell equation, 23 per cent.; Martin equation, 11·7 per cent.

Ammonia.				
		Mean 743.		*Mean 539.*
Chloroform .	737	— 6	529	— 10
Bromoform .	858	+ 115	614	+ 76
Carbon tetrachloride	813	+ 70	506	— 33
Amyl alcohol .	565	— 178	506	— 33

Average deviation from mean: Bell equation, 14 per cent.; Martin equation, 7 per cent.

To summarise the conclusions so far obtained :—

1. The hypothesis of a solute solvent interaction, not accounted for by the simple models, seems necessary in calculating energies of solution.
2. This interaction energy would appear to be very large for water as a solvent in comparison with other solvents.
3. The Martin equation is in better agreement with experiment than the equations either of Bell or Kirkwood after correction for interaction energy.
4. The slope of the $\Sigma\Delta F_0$, $1/D$ curve is characteristic of the solute alone, as required by the electrostatic model.

These conclusions are not meant to imply that the Martin equation is theoretically sound, but rather that it be accepted as a working method for estimating the electrostatic or " environmental " energy of solvation, from which, in conjunction with experimental data, it is possible to compute the interaction energy.

II. Additivity of Transference Energies.

An examination of the free energy of transfer calculated as described in Part I. from the less complete distribution data for the homologous series of fatty acids, reveals that this energy of transfer increases by an approximately constant amount for each additional CH_2 group and, furthermore, it would appear that the position of that CH_2 group has little or no effect, as exemplified by the case of butyric and iso-butyric acids, *cf.* cols. 3 and 4, Table IV.

TABLE IV.

Solvent.	1. $\Delta F\ \overline{\text{HAc}}$	2. (1-2).	$\Delta F\ \overline{\text{HPr}}$	(2-3).	3. $\Delta F\ \overline{\text{HBu}}$	(3-4).	4. $\Delta F\ \overline{i\text{-HBu}}$	(4-5).	5. $\Delta F\ \overline{i\text{-HVal}}$	(5-6).	6. $\overline{\text{HCap}}$.
Decalin . .	3141	1154	1987								
Benzene . .	2152	488	1664	778	886	101	987	606	321	1182	−861
Carbon tetra-chloride .	2490	582	1908	543	1365	240	1125	279	846		
Toluene . .	2186	356	1830	710	1120	−67	1187	707	480	1213	−733
Amyl alcohol .	+47	964	−917	476	−1393	+124	−1269				
Nitro benzene .	−305	−1259	954	349	605	88	519	673	−156		
Chloroform .			1086	711	375	30	345	642	−297	1151	−1430
Iso-prop. ether .			125	727	−602						
Ethyl bromide .			925								
o-Nitro toluene			1125	519	606			(3-5) 577	29		
Xylene . .			1668	574	1094				411		
Mean differences		708 *		598				590		1182 = 2 × 591	

* Neglecting anomalous value for EH_5NO_2.

In spite of the considerable divergencies from theory which exist when an alcohol is one of the solvents, the divergence is of the same magnitude for each acid, thus preserving an additivity which is more clearly illustrated by reference to Table IV. The data is taken from the papers of H. P. Smith[5] and N. A. de Kolossowsky.[6]

The same additivity is observed in the case of the α-Bromo fatty acids in Table V. Further examples are found in the measurements of England and Cohn[7] on the distribution of six amino acids between water and butyl alcohol. This data is shown in Table VI.

TABLE V.

Solvent.	1. $\alpha\mathrm{BrH}\overline{\mathrm{Ac}}$.	(1-2).	2. $\alpha\mathrm{BrH}\overline{\mathrm{Pr}}$.	(2-3).	3. $\alpha\mathrm{BrH}\overline{\mathrm{Bu}}$.	(3-4).	4. $\alpha\mathrm{BrH}\overline{\mathrm{Val}}$.
Toluene .	2151	973	1178	695	483	838	−355
EH_6 . .	1967	1047	920	716	204	703	−499
$CHCl_3$.			678	660	17·5		
Mean difference		1010		690		770	

TABLE VI.

Acid.	Glycine.		Alanine.		α-Amino-butyric.		Valine.		AminoH$\overline{\mathrm{Val}}$.		Leucine.		α-Amino-caproic.
$-\Delta F$ . .	2477		2186		1839		1559		1267		984		675
Difference .		291		347		280		292		283		309	

The energy of transference has been shown to arise from two sources. That which is the result of a change in electrostatic potential due to change in environment—" environmental energy," and that which is due to mutual interaction of the solvent solute molecules. That this latter should be an additive property of the molecule is reasonable, and Butler[8] has illustrated this principle with reference to the solution of the aliphatic alcohols in water. In the light of these results, the environmental energy change for a homologous series would appear to be constant for a series which shows additivity. Now the electrostatic potential depends (for any one solvent) on the dipole moment and on the dimensions of a hypothetical solid, assumed to surround the dipole. For the series of fatty acids, the dipole moment changes slowly as one proceeds up the series to butyric acid and thereafter is more or less constant. It would, therefore, appear that this hypothetical sphere containing the dipole, as required by the models of Martin and Bell, remains more or less constant for the series, and one is tempted to look upon the carboxyl group as being quite specific and isolated in its action. Reference to the table shows that the differences calculated for each CH_2 group between acetic and propionic acids, and for the α-bromo acids are not quite in line with the much greater constancy found for higher members. This is probably a reflection of the greater differences between the dipole moments which do exist amongst these lower members.

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[5] H. D. Smith, *J. Physic. Chem.*, 1929, **33**, 1964.
[6] N. A. de Kolossowsky, *Z. physik. Chem.*, 1934, **169**, 459.
[7] England and Cohn, *J.A.C.S.*, 1935, **57**, 635.
[8] Butler, *J.C.S.*, 1935, 280.

In other words, where we have molecules composed of polar groupings and non-polar groupings, it is probably a good approximation to consider these polar groups as being virtually isolated in their action and for a homologous series, specific. Similar conclusions have been reached by Martin and George[9] from a study of vapour pressures of solutions of benzyl alcohol and phenol. They deduced values for the radius of the hypothetical sphere which approached a common value, and were of the order of magnitude accepted for that of the hydroxyl group. The energy change accompanying the solution of long chain compounds will depend, therefore, mainly on those changes which accompany the solution of non-polar molecules, the electrostatic contribution becoming relatively less important.

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[9] Martin and George, *J C.S.*, 1933, 1413; *Trans. Faraday Soc.*, 1934, **30**, 759.

COMPLEX FORMATION.

By Geo. Glockler.

We are accustomed to consider various types of chemical compounds such as primary valency compounds which can be discussed and "explained" by the usual notions of valency and secondary valency compounds such as hydrates, ammoniates, etc., which are held together by secondary valency forces. These latter forces had to be invented *ad hoc* in order to explain the type of molecular compound which could not be dealt with by the simple valency theory. The further fact that molecules show tendencies to interact even though no definite compounds are formed required a further extension of our ideas. Gases are known to be imperfect, and we have invented "Van der Waals" forces to account for this interaction. The general scheme outlined has survived and even in the latest fashion, *i.e.* wave mechanics, the same situation is maintained. The language is different but we still separate the chemical, saturated valency forces from the van der Waals forces.

We wish to present here the argument that the division of these forces of interaction into chemical forces and van der Waals forces is in our opinion more a matter of convenience and of necessity only in so far as our ignorance demands simplification, rather than of fundamental significance.

Failure of Valency Theory.

For a satisfactory representation of our point of view we need to review some of the conspicuous inadequacies of the ordinary views of valency as held by the average chemist of to-day.

The Cubical Atom.—We may discuss the structure of chemical compounds at once on the modern picture of the cubical atom of G. N. Lewis.[1] However, on attempting to design a model of even as simple a molecule as acetylene we are in difficulty. It is quite impossible to construct a model of acetylene without considerable distortion of the carbon cubes involved.

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[1] G. N. Lewis, *Valence and the structure of atoms and molecules;* A.S.C. monograph; the Chemical Catalog Co. Inc., New York, 1923.

The Tetrahedral Atom.—A very natural distortion of the cubical atom leads at once to the tetrahedral atom of the organic chemists. This extension or change of the cubical atom was, of course, recognised by Lewis and the tetrahedral atom has since been used by many writers as a descriptive measure in the discussion of all primary valency compounds. The electron pair which takes such a conspicuous place as a representation of the valency bond in Lewis's theory is an even more prominent feature when the tetrahedral atom is used in a pictorial representation of chemical compounds.

Odd Molecules.—It is, of course, well known that the electron pair theory of valency is unable to account for odd molecules such as NO, and here we find an outstanding failure of the simple notions which otherwise permits the designation of hundreds of thousands of compounds.

The Hydrogen Halides.—We are certainly used to consider the position of a valency bond to be located between the two atoms which are considered as entities united by their valency bond, *i.e.* the electron pair. But how does this structural idea operate in the case of the hydrogen halides where we know that the distance between the nuclei is smaller than the diameter of the electron structure? Where we must then believe that the proton has entered the region of the negative halide ion! Again we see that the simple ideas of valency even as pictured on the electron conception are not sufficient for detailed description.

Oxygen Molecule.—It is very easy to draw a picture of the oxygen molecule on the notion of tetrahedral chemistry. We need only unite two tetrahedra by two sides, place a pair of electrons on each corner, indicating thereby a double bond of four electrons. Into the centre of each tetrahedron we place an oxygen atom nucleus and two *K*-electrons. Does this picture give a useful representation of the oxygen molecule? In many respects it is satisfactory, until we happen to think of the paramagnetism of the molecule and then we realise that the above naïve portrait is not complete. To be sure, modern detailed considerations involving the spin of the electrons give us an idea why in this case the usual spin neutralisation should not be complete and hence the paramagnetism is explained.

Pseudo-atoms; Isoelectronic Systems.—A very useful idea, which helps us in co-ordinating a great deal of chemical knowledge, is the concept of similarity of behaviour of molecules and radicals of the same number of electrons. The proposition can best be stated by giving a table due to Grimm[2] of some of the isoelectronic systems. A study of this table reveals a great deal of chemistry.

TABLE I.

C	N	O	F	Ne	Na^+
	CH	NH	OH	HF	$(NeH)^+$
		CH_2	NH_2	OH_2	—
			CH_3	NH_3	H_3O^+
				CH_4	NH_4^+
					—

The radicals in a column, for example, CH_3, NH_2 and OH are isoelectronic with fluorine. They form molecules by doubling up: $CH_3 - CH_3$, $NH_2 - NH_2$, OH — OH and F_2. Various systems of chemistry as, for example, the nitrogen system studied by Franklin[3] and others, are contained in the table: N, NH, NH_2 and NH_3. Organic chemistry is represented by: C, CH, CH_2, CH_3 and CH_4.

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[2] H. Grimm, *Z. Elektrochem.*, 1925, 31, 474.

Boron Hydrides.—The well-known difficulty of the structure of B_2H_6 is resolved when this problem is considered on the basis of Grimm's Table I. A complete system of chemistry of boron can be visualised by the addition of a diagonal line[4] containing the radicals: B, BH, BH_2, BH_3, BH_4 and BH_5. Ordinary valency theory and the electron conception were completely inadequate and could not yield a sensible structure for this remarkable hydride of boron: B_2H_6. On our basis, the structure of bor-ethane is obtained simply by considering the structure of the oxygen molecule given above, removing from the centres of the tetrahedra the oxygen kernels (*i.e.* the nuclei and their two K-electrons), and replacing these by boron kernels (*i.e.* boron nuclei with two K-electrons). It is seen that the picture presented here of bor-ethane does not allow us to draw any definite valency bond from the central boron atoms to any particular hydrogen atom. Rather the electronic structure of the molecule as a whole is to be considered with the positive kernels and protons embedded within.

Rare Gas Ion Hydrides.—The rare gases have no chemical properties in the usual sense, and this fact is expressed in the octet-theory by ascribing to this configuration very great stability. However, the evidence for the existence of rare gas ion hydrides is very definite,[5] and we can understand these structures on the basis of Table I. in connection with hydronium and ammonium ions. Ordinary views of valency are completely inadequate as a basis for consideration.

Co-ordination Compounds.—When we consider the great classes of compounds known as complex ion structures, we realise that the simple ideas of valency are entirely inadequate for the purpose of understanding their structure. We know that a given central ion can co-ordinate other ions and molecules, which have either a permanent dipole moment, or are highly polarisable. Many of these structures are very stable. The heat of formation per NH_3 of some ammoniates compares well in magnitude with the heat of formation of so-called primary valency compounds. Others again are very unstable as, for example, the polyhalides.[6]

The Interaction of Atoms.

Need it necessarily be possible to write a definite bond between a co-ordinating central ion and a co-ordinated molecule? It appears to us that considerations of energy seem to be more basic, and that this view as studied by Grimm and Herzfeld[7] for metals is the proper foundation for an understanding of valency. We may well ask the question: Is it not possible that a continuous series of structures exists which would begin with definite compounds such as sodium chloride and hydrogen, and which would end with systems which would ordinarily not be considered as chemical compounds at all? This idea can perhaps best be illustrated by Fig. 1.

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[3] E. C. Franklin, *The nitrogen system of compounds*, Reinhold Pub. Corp., New York, 1935.

[4] G. Glockler, *Science*, 1928, **58**, 305.

[5] K. T. Bainbridge, *Physic. Rev.*, 1933, **43**, 103; **44**, 57.

[6] A. E. v. Arkel and J. H. de Boer, *Chemische Verbindung als elektrostatische Erscheinung*, S. Hirzel, Leipzig, 1931.

[7] H. Grimm and K. F. Herzfeld, *Z. Physik*, 1923, **19**, 141.

Two Helium Atoms.—Even two helium atoms have a tendency to interact according to Eisenschutz and London,[8] and we can understand this situation, for we need only to recall that helium gas can be condensed to the liquid state, and in other words there are attracting forces acting. To be sure under ordinary conditions of temperature, impacts will prevent the formation of complexes of the type He : He, but let us consider the two helium atoms approaching each other and let us remove their energy at the position of equilibrium. Would the resulting system left to itself remain in the configuration He : He ? It would appear so, and we may well consider the complex to be a molecule. Of course we have driven the picture to an extreme, but it seems that we have learned at least caution, and we must recognise the fact that after all our definition of a molecule is arbitrary.

Definition of a Molecule.—The problem may be stated in another way. Can we separate the forces acting between atoms into two distinct categories where, in one group, we would claim that definite molecules can be placed, whereas into the second group the more indefinite complex interaction products would be located, usually termed van der Waals complexes. Or, again, should we make a clear distinction between chemical forces involved in fashioning chemical molecules and van der Waals forces operating in liquids and imperfect gases ? When we consider this question from the modern point of view we must answer it in the negative. For we should be able to treat any system by the solution of its wave equation

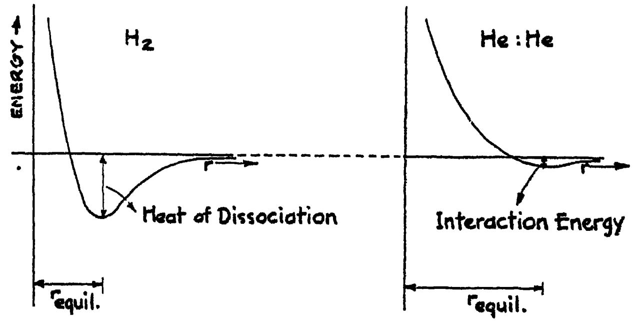

FIG. 1.

$$H\psi = W\psi$$

And how does the separation into and distinction of various forces arise ? It is because of our inability to solve the above equation exactly that we are forced to consider various approximations, which lead to a distinction between the forces acting between the component parts of the system. Were we able to solve the problem completely we should find that a certain configuration of the system would have a minimum energy and hence would be stable. The criterion of minimum energy seems to be the most important one for our considerations of really stable physical and chemical systems.[9]

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[8] R. Eisenschütz and F. London, *Z. Physik*, 1930, **60**, 520.
[9] G. Glockler, *J. Chem. Physics*, 1934, **2**, 823.

Complex Structures.

We should then consider liquids and other complexes of a similar nature as the representatives of one end of the series of structures mentioned above, which would contain members ranging all the way from very definite compounds which can be described very satisfactorily by the usual theories of chemical valency, and which would contain a pair of isolated helium atoms as an idealised limit at the other extremity of the series. The point of view represented here seems to be a very satisfactory basis for the discussion of many problems of chemistry which would otherwise appear as isolated cases.

Rare Gas Hydrates.—We would like to refer to the case of rare gas hydrates studied by Frocrand [10] and others who have shown that these gases, usually considered chemically completely inert, do form at high pressures, definite hydrates. On the basis of the attitude outlined above we feel not at all surprised that a dipole molecule like water should form some sort of complex structure with the more polarisable of the rare gases.

Hydrocarbon Hydrates.—Just as the rare gases form hydrates so do the saturated hydrocarbons.[10, 11] One would hardly think that such complex hydrocarbon hydrates are of technical significance, but the existence and stability of butane hydrate above the freezing-point of water caused freezing of valves in certain pipe-lines carrying gases from certain gas wells.

Quasi-molecules.—Oldenberg and others [12] have studied the spectra of certain molecular complexes formed from excited mercury atoms and rare gases or hydrocarbons. These loosely bound structures show certain banded spectra, and, in our view, are to be included into th egeneral series of complexes discussed above. Since they show band-spectra of a certain type one would be quite justified to designate them as molecules.

Coloured Molecular Compounds.—It is of further interest to refer to a study by Hunter and Northey [13] on the absorption spectra of mixtures of several quinones (chloroquinone, toluquinone, xyloquinone, and duroquinone) with various aromatic ethers, hydrocarbons and amines. They show that the various quinones are affected differently by the admixture of various substances. On the one hand we may have merely a " solvent effect" with little change of the absorption, and on the other hand very pronounced colour changes may happen, showing the " formation of molecular compounds," with all gradations in between these extremes. Again we find that this situation fits into the scheme outlined above.

Large Organic Molecules.—We ordinarily have the idea that the forces between atoms producing molecules are of larger magnitude than are the van der Waals forces holding molecules together in a liquid. While these relations may well represent the situation in numberless cases, we do find systems where the reverse may be true. If we consider some very large organic molecules, such as heavy hydrocarbons, proteins, etc., we are quite accustomed to the fact that they "decompose on melting" or heating. May we not suppose this situation to furnish us with an indication of the relative magnitude of the forces acting between atoms within molecules and between the molecules of the liquid? Can we not say that the van der Waals forces acting between the molecules are of sufficient magnitude to maintain the molecule within the liquid while the weakened intramolecular forces permit the rupture of the chemical bonds and hence the decomposition of the liquid consisting of these large molecules?

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[10] M. de Frocrand, *Compt. rend.*, 1902, **135**, 959.

[11] E. G. Hammerschmidt, *Ind. Eng. Chem.*, 1934, **26**, 851.

[12] O. Oldenberg, *Z. Physik*, 1929, **55**, 1 and G. Glockler and F. W. Martin *J. Chem. Physics*, 1934, **2**, 46.

[13] W. H. Hunter and E. H. Northey, *J. Physic. Chem.*, 1933, **37**, 875.

Summary.

1. Outstanding cases are cited which show that the usual views of valency are inadequate to deal with all chemical phenomena. Such cases are: the existence of odd molecules; the paramagnetism of oxygen molecule; the structure of boron hydrides, rare gas ion hydrides, etc.

2. It is proposed to classify all types of chemical compounds and complexes into a series of structures, which would contain definite chemical compounds on the one end and van der Waals molecules on the other. The energy of the compound or complex structure is the main consideration of its stability.

3. Complex structure such as rare gas hydrates, hydrocarbon hydrates, quasi-molecules, coloured molecular compounds, liquids and large organic molecules are considered as members of such a series of compounds and complex structures.

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THE ENERGY AND ENTROPY OF HYDRATION OF ORGANIC COMPOUNDS.

By J. A. V. Butler.

The most striking feature of aqueous solutions of organic compounds is the steady decrease of solubility which occurs in passing up a homologous series. It is obvious that appreciable solubility is conferred by certain hydrophyllic groups (—OH, —CO_2H, —NH_2, etc.) and the lower members of series of compounds are soluble in water in all proportions, but as the size of the hydrocarbon radicle increases a steady decreasing solubility occurs. The object of the work to be described here was to elucidate the factors which produce these effects.

In non-aqueous solutions it is usual to take Raoult's law as the standard and to express deviations from it by the activity coefficient $f = p/p^0 N$, where p is the partial pressure of a solute when its molar fraction is N, and p^0 the pressure of the pure liquid solute. In non-aqueous solutions f has usually quite moderate values, but in aqueous solutions effects of quite another magnitude are found. For example, the following are some of the values of f in dilute aqueous solutions at 25°: *n*-octyl alcohol, 12,300; ethyl chloride, *ca* 2000; di-propyl ether, 2×10^5; carbon tetrachloride, *ca.* 10^6.

The behaviour of a solute in a fairly concentrated solution is a very complex problem, for it depends not only on the interactions of the solute molecules with the solvent, but also with each other. The latter become less important as the concentration of the solute is decreased and are negligible in very dilute solutions. We shall discuss only the simpler problem of the behaviour of solutes in very dilute solutions, in which only the interaction of the solute with the surrounding solvent molecules need be taken into account.

Table I. shows the values of the activity coefficients of a series of aliphatic alcohols[1] in very dilute aqueous solutions ($N = ca.\ 10^{-3}$) which

[1] Butler, Thomson and Maclennan, *J. Chem. Soc.*, 1933, 674; Butler, Ramchandani and Thomson, *ibid.*, 1935, 280.

must be close to the limiting value for infinite dilution. These values were obtained either by the direct measurement of the partial pressure, or in the case of substances which are only slightly miscible with water from the solubility. In that case the partial pressure (p) of the saturated solution is nearly equal to the pressure of the pure solute (p^0) and $f = 1/N_s$, where N_s is the solubility. Even when the solute is completely miscible with water, f may be regarded as the reciprocal of the generalised solubility.

The activity coefficient f is not however the most suitable quantity by which to express the behaviour of the solute in a dilute solution, for it takes as the standard the pure liquid which is itself a complex state. Consideration of the figures in Table I. shows that the variations of f are to a considerable extent determined by the values of p^0, *i.e.* by the pure liquid. If we eliminate p^0 we are left with p/N, which is an expression of the distribution ratio of the solute between the vapour and the dilute solution.

TABLE I.—FREE ENERGIES, HEATS AND ENTROPIES OF HYDRATION OF ALIPHATIC ALCOHOLS AT 25°.‡

	$p/p^0 N$.	p^0.	p/N.	ΔF.	$-\Delta H$.	$-\Delta S$.
Methyl .	1·51	122·2	184	3·09	11·24	48·2
Ethyl .	3·69	59·0	218	3·19	12·88	54·0
n-Propyl .	14·4	20·1	291	3·38	14·42	59·7
iso-Propyl	7·7	44·0	339	3·45	13·45	56·7
n-Butyl .	52·9	6·78	360	3·49	15·94†	65·2
iso-Butyl	43·2	11·6	499	3·68	15·24	63·6
sec-Butyl	25·1	17·1	431	3·59	15·06†	62·6
tert-Butyl	11·8	42·4	503	3·69	14·44	60·8
n-Amyl .	214	2·50	532	3·73	17·50†	71·2
iso-Amyl .	191	3·11	593	3·78	—	—
sec-Amyl .	103	6·03	622	3·81	—	—
tert-Amyl	35	16·7	582	3·77	15·69†	65·3
n-Hexyl .	903	0·72	649*	3·84	—	—
n-Heptyl	3560	0·22	798*	3·96	—	—
n-Octyl .	12300	0·083	1020*	4·11	—	—

‡ ΔF and ΔH in *k* cals., ΔS in cals./degs.

This quantity increases in passing up the homologous series of alcohols, but to a small extent, *viz.* about one-fifth as rapidly as f. Thus of the observed decrease of solubility in passing from an alcohol to its next higher homologue, one-fifth is due to the interaction of the alcohol with water and four-fifths to the interaction of the alcohol molecules with each other in the pure liquid.

The Free Energy of Hydration.

It is convenient to express the distribution ratio of the solute between the vapour and solution in terms of the free energies in the two phases. If $F_g{}^0$ is the free energy of the solute vapour at unit pressure (1 mm. of mercury) and $\overline{F}{}^0$ its standard free energy in the solution as defined by $\overline{F} = \overline{F}{}^0 + RT \log N$, we obtain

$$\Delta F = \overline{F}{}^0 - F_g{}^0 = RT \log p/N. \quad . \quad . \quad . \quad (1)$$

This quantity may be termed the free energy of hydration of the solute. Although p/N is convenient in practice, a more natural expression of the distribution coefficient is in terms of the Ostwald coefficient $\lambda = c_l/c_g$, where c_l, c_g are the concentrations of the solute in the liquid and vapour in mols./c.c. When the standard states are defined in terms of these units, the free energy change is

$$\Delta F_c = RT \log c_g/c_l,$$

The relation between these expressions is

$$p/N = 1{\cdot}7032 \times 10^7 Td/273{\cdot}1\ M_1\lambda, \qquad (1)$$

where M_1 is the molecular weight of the solvent and d its density. For water at 25°, $p/N = 1{\cdot}028 \times 10^6/\lambda$, and therefore $\Delta F = \Delta F_c + 8200$ cals.

TABLE II.—FREE ENERGY, HEATS AND ENTROPIES OF HYDRATION OF ALIPHATIC COMPOUNDS AT 25°.

	p/N.	ΔF.	$-\Delta H$.	$-\Delta S$.
Methane	31·4 × 10^{6}*	10·23	3·18†	45·0
Ethane	23·0 × 10^{6}*	10·05	4·43†	48·6
Butane	5·0 × 10^{7}*	10·46	—	—
Ethylamine	421	3·58	12·91	55·4
n-Propylamine	530	3·72	—	—
n-Butylamine	639	3·83	—	—
Methyl acetate	3830	4·89	—	—
Ethyl acetate	5580	5·11	11·71	56·3
Propyl acetate	8380	5·35	—	—
Di-Ethyl ether	37200	6·24	12·76	63·7
Eth-Prop. ether	48200	6·39	—	—
Di-Prop. ether	147000	7·05	—	—
n-Propionitrile	1580	4·36	—	—
n-Butyronitrile	2190	4·56	—	—
Acetic acid	12·6	1·50	—	—
Propionic acid	18·5	1·73	—	—
n-Butyric acid	22·5	1·85	—	—
Acetone	5·79	4·29	10·09	48·3
Glycol	2·55	5·50	—	—
Glycerol	0·18	−1·01	24·72	80
Chloroform	—	7·14	9·8	57·0

* Derived from solubility. † From ΔF and its temperature coefficient.

The free energies of hydration of the compounds so far investigated are given, in terms of p/N, in Tables I. and II.[2] Table III. gives some of the values for straight chain compounds and shows that, in these

TABLE III.—FREE ENERGIES OF HYDRATION OF STRAIGHT CHAIN COMPOUNDS.

Radical (R).	RH.	$CH_3.CO_2R$.	RCN.	$R.NH_2$.	R.OH.	$R.CO_2H$.
CH_3	10·08	4·89	—	—	3·09	1·50
C_2H_5	10·00	5·11	4·36	3·58	3·19	1·73
C_3H_7	—	5·35	4·56	3·72	3·38	1·85
C_4H_9	10·46	—	—	1·85	3·49	—

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[2] Butler and Ramchandani, *J. Chem. Soc.*, 1935, 952.

compounds at any rate, the free energy is approximately an additive function of the groups in the molecule.

The average increment of ΔF for each additional — CH^2 group is about 160 cals. The values of the isomeric alcohols are somewhat greater than the corresponding straight chain compounds, and broadly speaking, F increases as the molecule becomes more compact.

The Heat of Hydration.

The free energy of hydration is determined by the heat and entropy of hydration, according to $\Delta F = \Delta H - T\Delta S$, where ΔH is the heat absorbed in bringing the solute molecule from the vapour into the dilute solution and ΔS the corresponding entropy change. We must therefore consider next to what extent the observed differences of ΔF are determined by the heat and entropy changes.

The heat of solution of the solute vapour at infinite dilution can be obtained from $\Delta H = \theta - Q$, where Q is the heat of vaporisation of the liquid solute and θ its heat of solution in water at infinite dilution. θ has been determined for a number of compounds, and Q can often be calculated from the vapour pressures. The values of ΔH obtained in this way are given in Tables I. and II. For some other compounds, marked †, for which these quantities are unknown, ΔH has been obtained from measurements of ΔF and its temperature coefficient[3] (see below).

The data at present available are very incomplete, and further measurements of the heats of solution of organic compounds in water are much to be desired. So far as can be seen from the values given, the heats of hydration are also additive in simple straight chain compounds. In the series of normal alcohols there is an increment in $-\Delta H$ of about 1·57 kilocals. for each additional — CH_2 group.

Some years ago Langmuir[4] gave an extremely interesting theory of solutions, based on his "principle of independent surface action," according to which the intermolecular energy of a solution is obtained by summing the various interfacial energies of the surfaces of contact of the molecules. On the assumption that the molecules are distributed completely at random, Langmuir derived expressions for the energy of transfer of molecules from their pure liquid to solutions of any concentration. Smyth and Engel[5] determined the partial pressures of a number of binary systems, designed to test this principle, but although there was a general qualitative agreement, quantitatively the deviations were considerable.

The assumption of a completely random distribution in both the pure liquid and the solution cannot be expected to be generally true. But in favourable conditions, particularly if only the transfer of the solute molecule from the vapour to a dilute solution is considered, it may give a satisfactory approximate method of dealing with solute-solvent interactions. The necessary conditions are (1) the interaction energy must be determined mainly by short range forces; (2) the arrangement of solvent molecules round one part of the solute molecule must not affect that round other parts. This is more likely to be satisfied when the solvent molecules are small compared with the solute molecules.

The process of bringing a solute molecule into a solvent may be supposed to consist of two steps; (1) making a cavity in the solvent large enough to hold the solute molecule; (2) introducing the solute molecule into the cavity. In the case of water, we can express the energy required to bring the solute molecule from the vapour into the solution as

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[3] Butler and Read. *J. Chem. Soc.*,1936, 1171.

[4] Langmuir, *Coll. Symp. Monographs*, 1925, 3, 48.

[5] Smyth and Engel, *J. Amer. Chem. Soc.*, 1929, 51, 2646, 2660.

$$\phi = \Sigma\gamma_{\mathrm{W-W}} - \Sigma\gamma_{\mathrm{A-W}} \quad . \quad . \quad . \quad . \quad (3)$$

where $\gamma_{\mathrm{W-W}}$ is the energy required to separate water molecules in order to make a cavity of the necessary size and $\gamma_{\mathrm{A-W}}$ the energy of interaction of the solute molecule with the water molecules at the surface of the cavity. The exact evaluation of this expression, taking into account the size and shape of the solute molecule, would be very difficult, but a simple approximation can be made in the following way. If we consider only the forces between adjacent molecules, (3) may be written as

$$\phi = n/2\ \gamma_{W-W} - \Sigma a\gamma_{A-W} \quad . \quad . \quad . \quad (4)$$

where γ_{W-W} is the energy required to separate a single pair of water molecules, and n is the total number of water molecules at the surface of the cavity, for we may suppose that in making the cavity $n/2$ water-water contacts are broken. γ_{A-W} is the energy of interaction of the group A of the solute molecule, with an adjacent water molecule, and a the number of water molecules adjacent to the group. In order to make a rough estimate of the value of these constants, we may suppose that water has on the whole the pseudo-crystalline tetrahedral arrangement suggested by Bernal and Fowler.[6] Thus, when a methane molecule, which does not differ greatly in size from the water molecule, is introduced into water, it may be supposed that there are four water molecules at the surface of the cavity and therefore

$$\phi_{CH_4} = 2\gamma_{W-W} - 4\gamma_{CH-W} \quad . \quad . \quad . \quad (5)$$

Similarly, the cavity of ethane will have six water molecules, and

$$\phi_{C_2H_6} = 3\gamma_{W-W} - 6\gamma_{CH-W} \quad . \quad . \quad . \quad (6)$$

Similar formulæ may be written for more complex compounds having groups, which are of comparable size, *e.g.*,

$$\phi_{C_4H_9\cdot OH} = 6\gamma_{W-W} - 9\gamma_{CH-W} - 3\gamma_{OH-W} \quad . \quad . \quad (7)$$
$$\phi_{(C_2H_5)_2O} = 6\gamma_{W-W} - 10\gamma_{CH-W} - 2\gamma_{OH-W} \quad . \quad . \quad (8)$$
$$\phi_{CH_3\cdot CO\cdot CH_3} = 5\gamma_{W-W} - 7\gamma_{CH-W} - 3\gamma_{O-W} \quad . \quad . \quad (9)$$

The heat of vaporisation of water at 25° is 10,500 cals. When a water molecule is removed from the interior of a mass of water, leaving a cavity, 4 water-water contacts are broken, and when the cavity is remade, two pairs of water-water contacts are remade, hence the heat of vaporisation corresponds to $2\gamma_{W-W}$ and $\gamma_{W-W} = 5{\cdot}25$. Hence, from (6), putting $\phi_{C_2H_6} = -4{\cdot}4$ k. cals., we obtain $\gamma_{CH-W} = 3{\cdot}36$.

The increment of ΔH for an additional — CH_2 group is in good agreement with this figure,

$$\Delta\phi_{CH_2} = \gamma_{W-W} - 2\gamma_{CH-W},$$

putting $\Delta\phi_{CH_2} = -1{\cdot}58$, we obtain $\gamma_{CH-W} = 3{\cdot}42$ k. cals.

In the same way we obtain the following energies of interaction of the various groups with water in straight chain compounds:—

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[6] Bernal and Fowler, *J. Chem. Physics*, 1933, 1, 515.

TABLE IV.—ENERGY OF INTERACTION OF VARIOUS GROUPS WITH EACH WATER MOLECULE (KILO-CALS.).*

γ_{W-W}	5·25	γ_{OH-W}	5·6	γ_{O-W} (ether)	5·1
γ_{CH-W}	3·4	γ_{NH_2-W}	5·6	γ_{O-W} (ketone)	4·1

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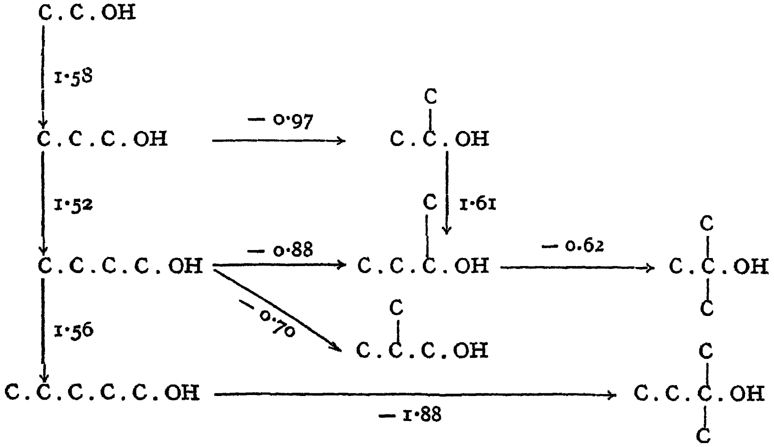
* These figures replace those given in *J. Chem. Soc.*, 1935, p. 954, which were based on the free energies of hydration.

It is significant that the interaction energies of the — OH and — NH_2 groups with water are somewhat greater than the water-water interaction, while those of the etheric and ketonic oxygens are somewhat less.

The heats of hydration of the isomeric alcohols are rather smaller than those of the corresponding straight chain compounds. The following table shows the differences of — ΔH between various structures:—



It can be seen that — ΔH decreases as the hydrocarbon group becomes more compact, and there is a drop of from 0·6 to 1·0 kilo-cals. in — ΔH for each branching of the chain. The average difference 0·8 is approximately equal to the energy change which would be produced, if the number of water molecules at the surface of the cavity were reduced by one for each branching of the chain. The following table shows the heats of hydration calculated on this assumption, using the constants of Table IV. *n* is the number of water molecules supposed to be in contact with the hydrocarbon group, and the total number at the surface of the cavity is *n* + 3. The agreement is probably within the experimental accuracy.

TABLE V.—OBSERVED AND CALCULATED HEATS OF HYDRATION.

	n	$-\Delta H$ (obs.)	$-\Delta H$ (calc.)		*n*	$-\Delta H$ (obs.)	$-\Delta H$ (calc.)
$CH_3.CH_2.CH_2OH$.	7	14·42	14·4	$CH_3.CH(CH_3)CH_2OH$	8	15·24	15·1
$(CH_3)_2CHOH$ . .	6	13·45	13·6	$C(CH_3)_3OH$ . .	7	14·44	14·4
$CH_3.CH_2.CH_2.CH_2OH$	9	15·94	15·9	$CH_3(CH_2)_3CH_2OH$.	11	17·50	17·5
$CH_3.CH_2.CH(CH_3)OH$	8	15·06	15·1	$CH_3.CH_2.C(CH_3)_2OH$	9	15·69	15·9

The Entropy of Hydration.

The heat of hydration is not however the predominant factor determining the free energy. An examination of Table I. shows that in a homologous series of compounds ΔH and ΔF change in *opposite directions*. The entropy of solution, which is equal to $\Delta S = -(\Delta F - \Delta H)/T$ therefore changes considerably from one compound to another. This has a most important effect on the series of vapour solubilities, for if the entropy were a constant this quantity (N/p) would increase in a homologous series, instead of decreasing.

The entropies of hydration are given, where the data exist, in Table I. They are obtained[8] (1) from ΔF and the thermochemical value of ΔH; (2) from the temperature coefficient of ΔF, by $d(\Delta F)/dT = -\Delta S$. If the free energy is defined in terms of the concentrations of the solute in the two phases (p. 231), the corresponding entropy change differs from that given by

$$\Delta S_c = \Delta S + 29{\cdot}4,$$

in cals./degs. for water at 25°. The entropies of hydration of a number of gases, calculated from their solubility are given in Table VI.

TABLE VI —HEATS AND ENTROPIES OF SOME GASES AT 25° C.

	$-\Delta H$.	$-\Delta S$.		$-\Delta H$.	$-\Delta S$.		$-\Delta H$.	$-\Delta S$
H_2	1·28	39·2	N_2	2·14	43·0	CH_4	3·18	45·0
He	1·02 (0·53)*	40·0 (38·6)*	O_2	2·99	44·5	C_2H_6	—	48·6
Ne	1·88 (0·85)	42·0 (39·4)	CO	3·91	43·0	C_2H_4	3·79	44·5
A	2·73 (2·63)	43·4 (43·1)	CO_2	4·73	43·8	C_2H_2	3·36	38·8
Kr	3·55	45·5	COS	5·80	48·3	CH_3Cl	6·3	46·8
X	4·49	46·8	NO	2·68	42·6	(CCl_4	6·9	51)
Rn	5·05	47·5	N_2O	4·84	44·8			

* The bracketed figs. for the inert gases are from Lannung's measurements (*J. Amer. Chem. Soc.*, 1930, **52**, 73), and the remainder from Valentiner's interpolation formulæ (Landolt-Börnstein).

Bell[7] has pointed out that in certain organic solvents there is a linear relation between the entropies of the solution of gases and their heats of solution. With "non-polar" solutes in water the entropy of solution also increases with the heat of solution (Fig. 1), and the deviations from a linear relation in most cases are probably not greater than the experimental uncertainty. There is also a linear relation between the entropies and heats of hydration of the alcohols, but it does not coincide with that of the "non-polar" solvents.

The origin of these effects is not clear. Our suggestion[8] that the value of $-\Delta S$ is related to the size of the cavity containing the solute molecule is not very well borne out by the more extensive data now given. The entropy is a measure of the number of possible configurations of the system having a given energy. When the solute molecule is brought into the field of force of the solvent there may be some restriction of its possible configurations, which will lower the entropy, and this effect might well be proportional to the energy of interaction of the solute with the solvent. Conversely the solvent molecules round the solute will be affected in the same way, and any change of entropy which arises therefrom will appear in the partial entropy of the solute.

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[7] Private communication.

Whatever may be the origin of this effect, the presence in the solute molecule of hydroxyl and similar groups which form " hydrogen bonds "

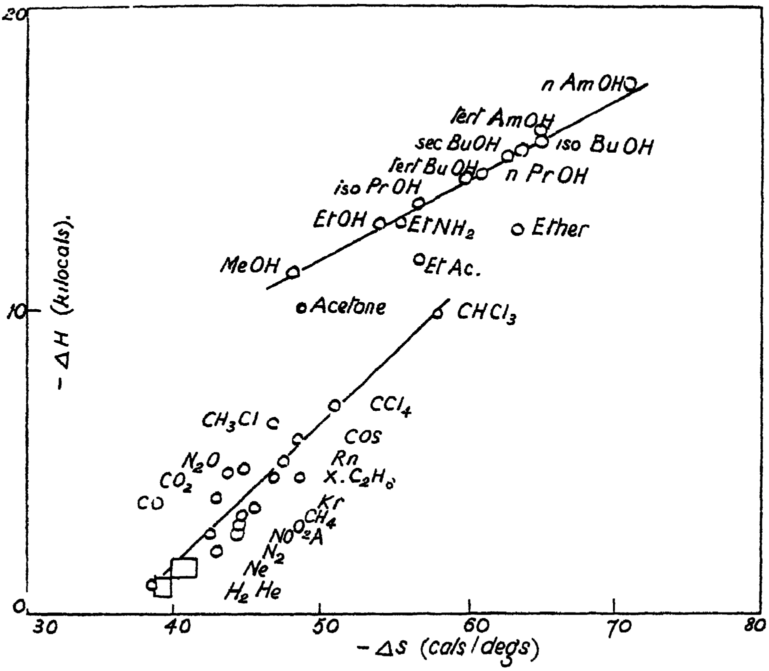

FIG. 1.

with water evidently introduces a new factor, which increases the partial entropy in solution as compared with non-polar compounds having the same heat of solution. It may be observed that linear relations between the heats and entropies of hydration have also been found in the case of gaseous ions.[8]

Summary.

1. A discussion is given of the free energy, heat and entropy of hydration of the simpler organic compounds in water. The heats of hydration are additive for simple compounds, and the energies of interaction of various groups with water have been estimated.

2. The entropies of hydration of non-polar molecules vary roughly linearly with the heats of hydration. A linear relation which does not coincide with this is also found for the aliphatic alcohols.

King's Buildings,
West Mains Road,
Edinburgh.

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[8] Latimer and Buffington, *J. Amer. Chem. Soc.*, 1926, 48, 2297.

GENERAL DISCUSSION.

Mr. C. R. Bury (*Aberystwyth*) said: Is the assumption of random distribution in solutions of alcohols in water justifiable? Langmuir's principle of independent surface action is—as Butler's works shows—inconsistent with random distribution, and in recent years I have obtained fairly conclusive evidence for mixtures of butyric acid and water, that the two types of molecule are segregated to some extent—that there is what Professor Prins would call a " sub-arrangement." To what extent is the accuracy of Dr. Butler's calculations vitiated by the assumption of random distribution?

Dr. G. Salomon (*Reading*) said: The halogen alkylamines,

$$Cl—CH_2—(CH_2)_{n-2}—CH_2—NH_2,$$

are liquids miscible with water. The lower members of the series are completely miscible. For $n = 5$ the solubility certainly exceeds 1 mol./litre, but when $n = 6$ the solubility suddenly drops,[9] by more than two hundred-fold, to 0·005 mols./litre. The point of appearance of a visible emulsion readily gives a rough idea of the degree of insolubility. For a more exact estimation, a simple kinetic treatment,[10] depending on the tendency of the base to polymerise, exhibited also when in sub-microscopic drops, is of service.

This effect may readily be interpreted with the aid of Langmuir's Principle. For $n = 5$, the hydrophilic power of the amino-group preponderates, as opposed to the hydrophobic power of the alkyl residue, but when $n = 6$ this is no longer the case. For the latter member of the series however, the molecule must favour the closed form, because in that, according to Langmuir, the alkyl residue presents the smallest surface area to water. This explanation does not suffice by itself, however, to interpret the sudden drop in solubility, for, indeed, the molecule in the closed form, with $n = 6$, has a surface area hardly bigger than that of the open form with $n = 5$.

In order to understand these unexpected results, one must rather take the view that, in the closed form, the halogen alkyl- and amino-groups have a reciprocal action upon each other, whereby the hydrophilic power of the amino group is to some extent diminished and the water solubility of the substance correspondingly reduced. It should be possible, with the help of the data communicated by Dr. Butler and of Langmuir's calculations, to treat the experiments quantitatively.

Finally: is it possible, using Dr. Butler's data, to estimate the number of water molecules tightly bound to a hydrophilic group and to compare it with the number only loosely bound? The solution of these problems would be of the greatest service in answering many questions in colloid chemistry.

Dr. J. D. Bernal (*Cambridge*) said: The results contained in this paper seem to me to be of great importance, as they show to what extent simple considerations of interatomic forces can lead to quantitatively exact results for energies of hydration. The methods are essentially the same as those I used for the calculation of the heats of hydration of ions, but I never expected that they could be used with such success for far more complicated compounds. The objections that have been raised on the grounds of the failure of the still higher homologues to fit into the scheme can, I think, be explained by a definite formation of associated groups here, of course, attached together by their hydrophobic portions. These groups may be bi-molecular, but in most cases the physical evidence would seem to point towards the existence of much larger groups tending towards definite colloidal aggregates.

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[9] *Trans. Faraday Soc.*, 1936, **32**, 161.

[10] *Helv.*, 1936, **19**, 762.

Professor F. G. Donnan (*London*) said: In the case of the micellar aggregates in aqueous solutions investigated by Bury and by Hartley [11] it would seem that Dr. Butler's method of estimating the interaction between water molecules and atoms or atomic groups would break down. Possibly this might provide a new method of investigating such systems.

Professor J. A. Prins (*Wageningen*) said: Dr. Bernal raised the question at what chain length a clustering of fatty and/or alcohol molecules in water would begin. The results mentioned by Mr. Bury above indicate that this is already the case with the comparatively short molecules of butyric acid.

Dr. J. A. V. Butler (*Edinburgh*), in reply said · In reply to Mr. Bury, random distribution almost certainly cannot be expected in most moderately concentrated solutions, but in the work described we have limited ourselves to very dilute solutions and solutes with which it is reasonable to suppose that no appreciable aggregation occurs at these concentrations Our object has been to find the energy, etc., of interaction of the isolated solute molecule with water and the methods employed only give this when the solute is molecularly dispersed in the solutions used. In the cases mentioned by Professor Donnan we should not be able to find the energy of interaction of a single molecule with water. But the additive relations we have obtained would make it possible to estimate the energy of interaction of the higher fatty acids from the values of the lower members, and from the energy of solution in an actual solution we could then find the energy of the aggregation process.

With regard to Dr. Bernal's remarks, I think it is not quite right to speak of the failure of the scheme with higher homologues. So far as I can see, there is no need to expect that the scheme will fail in such cases, but there is an additional factor, *viz.*, the aggregation phenomenon, to be taken into account which may be important at quite low concentrations.

The anomalous solubilities of the halogen alkylamines mentioned by Dr. Salomon might arise either from peculiarities in the pure liquid state or from the behaviour of the aqueous solutions. It would be interesting to have the vapour pressures of these compounds so that the vapour solubilities might be determined. In the aliphatic alcohols there is no discontinuity in the solubility at the point at which a ring configuration becomes possible, but the introduction of a halogen atom at the other end of the chain might change this. It should be remembered that the change to a ring configuration would be associated with a change in the entropy of solution which might have a greater effect on the solubility than the energy difference.

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[11] Compare, for example, *Aqueous Solutions of Paraffin Chain Salts*, by G. S. Hartley; No. 387 of the *Actualités scientifiques et industrielles*, published by Hermann & Cie, Paris.

EFFECT OF IONIC FORCES SHOWN BY THE LIQUID STRUCTURE OF ALKALI HALIDES AND THEIR AQUEOUS SOLUTIONS.

By G. W. Stewart.

University of Iowa. *Received* .

Experimental evidence of the past nine years, more particularly in X-ray diffraction, has given a growing confidence in the fact and significance of semi-orderly structure in liquids. But the existence of mobility has thus far rendered quite impossible the determination of a fairly exact description of the nature of the structure of any liquid. At this stage of our knowledge, experimental evidence of liquid structure from all angles is highly desirable. This paper utilises the opportunity to collect certain established alkali halide data which seem to give interesting evidence of the carry-over into the liquid state of some structural effects. Additional data also suggest certain tentative views concerning the effect of the alkali and halogen ions in aqueous solutions.

I. (a) Ratio of Solid and Liquid Densities.[1]

Table I. gives the ratio of densities of the solid alkali halides at room temperature to that of the liquids just above their melting-points. All temperatures, other than room temperature, are indicated in parentheses. Unfortunately the author has not been able to find data for the solid densities, ρ_S, near the melting-point. Also, there is no available information covering the crystal structure of these halides over the range of temperature from 20° to their respective melting-points. It may be pointed out, however, (1) that the values of ρ_L were all taken at very roughly the same distance from the melting-point, 600° to 900° C., and (2) that the temperature coefficient of ρ_S at room temperature is practically the same for all (Li group and all fluorines not known), with that of the Na, K, and Rb groups varying at most 20 per cent. and of the Cs group less than 10 per cent. If the lower temperatures were at equal distances from their respective melting-points, the comparison would be improved, but the change resulting from this would probably not alter the values of ρ_S/ρ_L in Table I. by much more than perhaps 7 per cent. Making allowance for the unsatisfactory character of the data, there are yet several apparently significant comparisons of the values of ρ_S/ρ_L which may be enumerated as (see Table I.).

(1) The ratios, ρ_S/ρ_L, are surprisingly constant for any one alkali, the variation for the four, Li to Rb, being from a mean value respectively, 3·3, 2·7, 1·1 and 3·2 per cent. All of these have the NaCl structure.

(2) The CsF has the same structure, but the other caesium halides have the body centred cubic or the CsCl structure. If now the calculation were made as if all the caesium halides had the sodium chloride structure [2] then the ratios, ρ_S/ρ_L, for the chloride, bromide and iode, would be 1·19, 1·19 and 1·19 respectively. This would cause the variation from a mean value of ρ_S/ρ_L for the caesium halides of 2·5 per cent. Or if the CsF is assumed to have a CsCl structure, its ρ_S/ρ_L would be 1·51, and the corresponding variation would be the same.

(3) There seems to be no traceable relation between ionic radii ratios and the values of ρ_S/ρ_L. For example, the greatest constancy of ρ_S/ρ_L exists for the potassium halides and the least for the rubidium and sodium halides. Yet with the rubidium case the radii ratios are nearer unity than with potassium. Again, the change in radii ratio KF to NaF is approximately the same as from KF to KBr, yet the ρ_S/ρ_L differs by 10 per cent. in the former case and less than 2 per cent. in the latter. Other similar comparisons may be made. If the change was from a characteristic NaCl type of structure, in the case of the first four groups of halides, to a liquid packing of a random type, then the influence of the ratios, r_1/r_2, might be expected to be detected, but is not.

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[1] The attention of the author was first directed to the data in Table I. and Fig. 1, by Dr. Linus Pauling. The benefit of conversations with Dr. Pauling covering the entire content of this report is also acknowledged.

[2] The change in density, according to Pauling, *Z. Krist.*, 1928, 69, 35, would require the factors, 0·84, 0·841, and 0·846 respectively.

TABLE I.*

		F	Cl.	Br.	I.
Li	ρ_S	2·65	2·06	3·46	4·09
	ρ_L	1·802 (842°)	1·498 (606°)	2·546 (549°)	—
	ρ_S/ρ_L	1·47	1·37	1·36	—
	r_1/r_2	0·441	0·331	0·308	0·278
Na	ρ_S	2·81	2·16	3·24	3·67
	ρ_L	1·949 (988°)	1·549 (800°)	2·335 (740°)	2·739 (661°)
	ρ_S/ρ_L	1·44	1·40	1·39	1·34
	r_1/r_2	0·698	0·524	0·487	0·439
K	ρ_S	2·53	1·99	2·76	3·12
	ρ_L	1·914 (846°)	1·528 (768°)	2·124 (728°)	2·450 (682°)
	ρ_S/ρ_L	1·32	1·30	1·30	1·27
	r_1/r_2	0·978	0·735	0·682	0·616
Rb	ρ_S	3·87	2·81	3·37	3·57
	ρ_L	2·921 (725°)	2·115 (717°)	2·709 (681°)	2·863 (642°)
	ρ_S/ρ_L	1·32	1·33	1·24	1·25
	r_1/r_2	1·09	0·818	0·759	0·685
Cs	ρ_S	4·62	4·00	4·45	4·51
	ρ_L	3·583 † (723°) 3·631 (684°)	2·812 (626°)	3·156 (627°)	3·198 (621°)
	ρ_S/ρ_L	(1·27)	1·42 (1·19)	1·41 (1·19)	1·41 (1·19)
	r_1/r_2	1·24	0·933	0·866	0·782

* ρ_S is the density of the solid, ρ_L of the liquid and r_1 and r_2 are the Pauling ionic radii (*Z. Krist.*, 1928, **67**, 377) of alkali and halogen, respectively, and are given in Table III.

All temperatures are in °C. The densities of solids are computed from the crystal data given in *Int. Crit. Tables*, Vol. I. pp. 342-346, with the addition of the size of unit cell for RbF as given by Wyckoff, *The Structure of Crystals*, 1931 edition.

All densities of liquids are from Landolt and Börnstein, *Ergäanz*, I., p. 210.

† *Int. Crit. Tables*, IV., p. 446.

Since density depends upon structure, the constancy of the ratio ρ_S/ρ_L for the alkali series in each case (crystal structure considered) may be regarded as evidence that the forces producing the crystal structure, the interionic distances and indirectly the density, still have in the liquid a similar characteristic indirect influence upon the density. The presence of the alkali seems to determine this characteristic effect.

(b) Anomalies at the Melting- and Boiling-Points.

Fig. 1 is taken directly from Pauling's [3] discussion of anomalies at the melting- and boiling-points of the alkali halides. He discusses the influence of the relative ionic sizes on these two transition temperatures. By the use of perturbation, polarisation neglected, he determines this influence. He then establishes a corrected value of interionic distance which would occur if the radius ratio effect did not exist. From these corrected distances and the use of Trouton's rule for the melting-point and Richard's rule for the boiling-point, he shows that, without the radius ratio effect, the new melting- and boiling-points would cease to show the irregularities in Fig. 1, wherein the Li values and the NaI value seem to be anomalous. Then the lines connecting the melting-points, and similarly the boiling-points, would not cross, and the order would always be Li, Na, K, Rb, and Cs. Pauling's discussion emphasises the fact that the interionic forces which are responsible for crystalline structure characteristically and similarly affect the temperatures of melting and boiling. For the purposes of this paper, however, we need only notice that the anomalies of melting-points and boiling-points are strikingly similar, though the transition in one case is from the solid and the other from the liquid. This indicates quite directly the significance of the carry-over of structure from solid to liquid and its at least partial retention to the boiling-point. The characteristic X-ray diffraction at the boiling-point of a liquid has previously been noted.[4]

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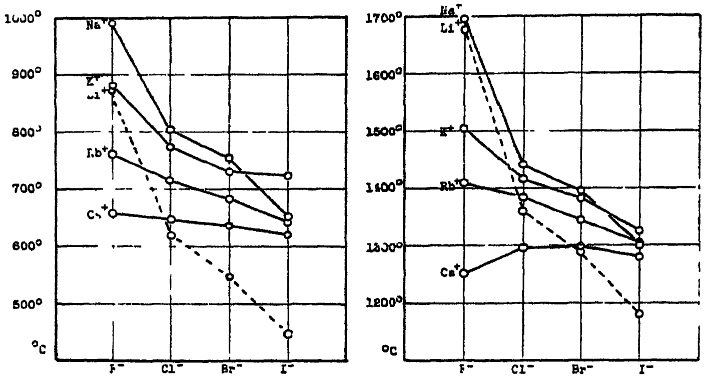
[3] Pauling, *J. Am. Chem. Soc.*, 1928, **50**, 1036.



(a) (b)

Figure 1.
Melting (a) and boiling (b) points of alkali halide.

II. Volume Effects in Aqueous Solutions of the Alkali Halides.

Volume effects of the alkali halides in aqueous solutions have been studied experimentally and theoretically in much detail. Masson[5] found that the apparent molal volume of electrolytes in aqueous solution increased with the square root of the concentration. The rule may be stated as follows:

$$\phi = kc^{\frac{1}{2}} - \phi^{\circ}$$

where ϕ is the apparent molal volume, c is concentration in gram moles per litre of solution, and k and ϕ° are constants for each electrolyte. This square root rule has some theoretical justification[6] based on the Debye-Hückel theory, but this is negatived in that its agreement with experiment is not limited to electrolytes,[7] that it does not seem to apply to dilute solutions with improved data, and that k does not have the dependence upon the type of valence as specified by the theory.[8] The apparent compressibilities and minimum values of the apparent molal volumes have also been the subject of discussions based on Masson's rule.[9] But it cannot be said that the explanations of the apparent volumes of ions and non-electrolytes in water are satisfactory. The purpose of this paper is to direct attention to certain data which seem to add confidence that the "quasi-crystalline" or "cybotactic" structure of the solute, water, must enter importantly into future satisfactory explanations. The data have been computed from those in the *Int. Crit. Tables*, Vol. III., pp. 77-94. While more accurate measurements have been made of densities of alkali halide solutions[10] yet those selected as stated are sufficiently satisfactory for the purpose of this paper. For with the smallest concentration used, an error of 4 in the last significant figure in the density data would cause a 1 per cent. error in Δv, the value to be discussed, and this is the maximum error in computed values. 1, 2, 4, 10 and 20 per cent. concentrations, grams of ions per 100 grams of solution, were used. For each concentration, the apparent volume per ion pair, Δv, was computed. The data for fluorine were omitted because unknown. $v_1 + v_2$ is the sum of ionic spheres using Goldschmidt radii, this arbitrary sum giving a means of comparison with the experimental Δv, the ratio of the latter to the former being a convenient value for the purpose. For simplicity the Δv's are given only for a single concentration, but the ratios for all.

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[4] *E.g.*, Skinner, *Physic. Rev.*, 1930, **36**, 1625-1630.

[5] Masson, *Phil. Mag.*, 1929, **8**, 218.

[6] Redlich and Rosenfeld, *Z. physik. Chem.*, 1931, **155**, 65.

[7] Scott and Wilson, *J. Physic. Chem.*, 1934, **33**, 951, and other papers.

[8] Scott and Bridge, *ibid.*, 1936, **40**, 461.

In the view of this article, the ions modify the liquid structure of the solvent in a region much larger than the immediate neighbourhood of the ion. The effect per pair of ions will undoubtedly depend upon their size as well as the total number of them per c.c. It will also vary with the identity of the ions themselves. In the absence of knowledge or even reasoned conjecture, no one method of comparing the Δv's is decidedly preferable. Table II. compares the apparent volume per ion pair with the sum of the two ionic spheres, but does not regard the difference in number of these pairs per c.c. If one takes this omission into account and selects that concentration in each case which will give the same total volume of ionic spheres per c.c., there is no material change in the conclusions drawn by the other selection. The second method is represented in Table II. by the ratio for "eq. vol.". It might also be noted that if the Δv's are divided between the two ions of a pair, the conclusions are essentially the same. But in so doing the hydration of one of a pair would be neglected. In Table II. are to be observed the following:

(1) Two facts not new, one readily seen from Masson's empirical rule, are, firstly, the increase of Δv with concentration and, secondly, its more rapid increase with molecules of lesser weight when concentration percentage is expressed in weight.

(2) At any of the concentrations, the ratio values, $\Delta v/(v_1 + v_2)$, seem to be divided approximately into three groups, (1) lithium and sodium halides; (2) potassium and rubidium halides; and (3) caesium halides.

(3) This ratio for any concentration has a greater constancy in an alkali row than in a halogen column.

(4) The constancy for the ratio values is greatest for K, Rb and Cs rows and least for the Na row.

Any conclusions reached from the values of $\Delta v/(v_1 + v_2)$ in Table II. must, of course, depend upon the significance of this ratio. While its trial use seems entirely reasonable if one wishes to bring to light any difference in effect of the ions on the solvent, yet one must be influenced

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[9] Scott and Wilson, *loc. cit.*[7]

[10] Scott, Obenhaus and Wilson, *J. Physic. Chem.*, 1934, 38, 931.

TABLE II.

		Cl r_2=1·81 v_2=24·8	Br =1·96 =31·5	I =2·20 =44·6
Li r_1 = 0·78 v_1 = 1·99	$v_1 + v_2$	26·8	33·5	46·6
	Δv	28·9	39·5	57·4
$\Delta v/(v_1 + v_2)$ for	1 %	1·08	1·18	1·23
,,	,, 2 ,,	1·10	1·20	1·25
,,	,, 4 ,,	1·13	1·21	1·26
,,	,, 10 ,,	1·19	1·24	1·27
,,	,, 20 ,,	1·25	1·27	1·29
,,	eq. vol.	1·16	1·25	1·28
Na r_1 = 0·98 v_1 = 3·94	$v_1 + v_2$	28·7	35·4	48·5
	Δv	27·8	37·8	56·4
$\Delta v/(v_1 + v_2)$ for	1 %	0·967	1·06	1·16
,,	,, 2 ,,	0·990	1·09	1·18
,,	,, 4 ,,	1·02	1·12	1·19
,,	,, 10 ,,	1·09	1·16	1·21
,,	,, 20 ,,	1·17	1·20	1·23
,,	eq. vol.	1·09	1·18	1·23
K r_1 = 1·33 v_1 = 9·85	$v_1 + v_2$	34·7	41·4	54·5
	Δv	44·0	55·0	73·2
$\Delta v/(v_1 + v_2)$ for	1 %	1·27	1·33	1·34
,,	,, 2 ,,	1·30	1·35	1·36
,,	,, 4 ,,	1·33	1·37	1·37
,,	,, 10 ,,	1·38	1·40	1·39
,,	,, 20 ,,	1·44	1·44	1·42
,,	eq. vol.	1·38	1·42	1·40
Rb r_1 = 1·49 v_1 = 13·9	$v_1 + v_2$	38·7	45·4	58·5
	Δv	52·3	62·7	81·0
$\Delta v/(v_1 + v_2)$ for	1 %	1·35	1·38	1·39
,,	,, 2 ,,	1·37	1·41	1·41
,,	,, 4 ,,	1·40	1·43	1·42
,,	,, 10 ,,	1·42	1·45	1·44
,,	,, 20 ,,	1·47	1·48	1·46
,,	eq. vol.	1·45	1·47	1·45
Cs r_1 = 1·65 v_1 = 18·8	$v_1 + v_2$	43·6	50·3	63·4
	Δv	63·8	74·4	92·5
$\Delta v/(v_1 + v_2)$ for	1 %	1·46	1·48	1·46
,,	,, 2 ,,	1·48	1·50	1·49
,,	,, 4 ,,	1·50	1·52	1·50
,,	,, 10 ,,	1·53	1·54	1·52
,,	,, 20 ,,	1·56	1·57	1·54
,,	eq. vol.	1·56	1·57	1·54

r_1 and r_2 Goldschmidt ionic radii in Å.u. alkalis and halogens, respectively.

v_1 and v_2, spherical volumes, $\frac{4}{3}\pi r_1^3$, and $\frac{4}{3}\pi r_2^3$, respectively.

Δv, apparent volume in (Å.u.)^3 of a pair of ions.

Equal volumes refers to equal total spherical volumes ($v_1 + v_2$), in equal volumes of the solution, the former being that of the 20 per cent. CsCl.

by the results reached thereby. The most striking feature is the constancy of the ratios for any one alkali. This makes a discussion of Table II. seem worth while.

That the water has a significant structure is now rather widely accepted[11] and need not be discussed in any detail. The influence of ions in altering this structure of the solvent is also not experimentally new.[12] If the effect of an ion on the water structure is not merely in the immediate neighbourhood of the ion but extends,[13] with decreasing magnitude, to at least a distance extending over perhaps a ten or more molecules of water, then the gradual increase of volume Δv with increase of concentration is at once visualised. For the effect on the water structure in the cases herein cited, is to increase its density or to decrease its volume. The more sparse the ions, the greater the total decrease in water volume produced by a single pair of ions. As the density of ions becomes greater the structure of the water becomes more uniformly altered, approaching a "saturation" density effect, and hence placing less and less shrinkage responsibility upon one ion pair. With 1 per cent concentration by weight and with the heaviest ion pair in Table II., CsI, the ratio of number of molecules to that of water is 1 : 2400, giving the separation of two Cs ions as a distance extending over approximately 10 water molecules. It may be remarked that the extended effect on the water structure here emphasised may explain the "super-structure" of ions [14] in solution. For clearly this extension will indirectly influence the relative positions of neighbouring ions. Another way of expressing the same view is to describe the ions as participants with the water in one common or shared structure, though not a homogeneous one. Experiments with solutions have indicated [15] that the mechanism of solution is one of forming a common liquid structure different from that of either constituent.

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[11] Bernal and Fowler, *J. Chem. Physics.*, 1933, **1**, 515.

[12] See references to Prins, Meyer, and Good in Stewart, *J. Chem. Physics.*, 1934, **2**, 147, and Bernal and Fowler, *loc. cit.*[11]

[13] The general idea of this extension of effect was stated by Bernal and Fowler, *loc. cit.*

The three groups mentioned in "2," occurring for any of the concentrations, may seem to be accounted for (1) by hydration of the Li and Na halides, and (2) by the difference in crystal structure of the caesium and of the potassium and rubidium halides. According to the view of Bernal and Fowler,[11] Li^+, Na^+, K^+ and F^- are permanently hydrated in the solution as in crystals, Li^+ with 6, and Na^+ with 8 water molecules. They also conclude that the other ions in Table II. are 4-co-ordinated in water solution. The difference of effect of the 4, 6 and 8 are perhaps indicated in Table II. by the decreasing ratio, $\Delta v/(v_1 + v_2)$. Thus the first explanation of conclusion "2," namely hydration, seems to be fairly satisfactory. But why are the ratios with potassium and rubidium halides so nearly the same and noticeably different from the ratios with the caesium halides? The suggestion that these similarities and differences may be accounted for by any crystal characteristic carried over into the ionic solution, seems a little fanciful. Yet one must face the two facts, first that an alkali seems to be the more responsible for the difference between the body centred CsCl structures and the simple cubic structure of the remaining halides and second, that the constancy of $\Delta v/(v_1 + v_2)$ follows the alkalis and not the halogens. The results in the ionic solution are as if the forces which produced a difference in crystal structure now produce a difference in water structure. It is at least an interesting conjecture, probably capable of test by experiment.

In presenting the above description of the action of the ions in the solvent, it becomes evident that this view does not immediately provide an explanation of all the known facts, for example, of the increase in Δv caused by pressure.[16] This effect is not large, in one case increasing the ϕ° or the constant in Masson's linear rule, from 17·0 to 21·9 by a change from 1 to 2000 atmospheres. At the same time, there seems to be nothing contradictory in this or any other experiment to the view here emphasised. There is as yet no satisfactory explanation of the facts, and quantitative discussions have had dependence only upon the empirical Masson's rule. The only object of this section of the paper is to present the possible significance of Table II. for consideration in future studies of the very complex situation in electrolytic solutions.

The above interpretation requires that with a positive rate of change of apparent volume per ion pair with increased concentration, the effect

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[14] Prins, *J. Chem. Physics*, 1935, 3, 72; and Prins and Fontegue, *Physica* II, 1935, 1016.

[15] *E.g.*, Meyer, *Physic. Rev.*, 1931, 38, 1038.

[16] Adams, *J. Am. Chem. Soc.*, 1931, 53, 3769, and 1932, 54, 2229.

TABLE III.

		Cl r_2=1·81 v_2=24·8	**Br** =1·95 =31·0	**I** =2·16 =42·3			**Cl** r_2=1·81 v_2=24·8	**Br** =1·95 =31·0	**I** =2·16 =42·3
Li r_1 = 0·60 v_1 = 0·906	$v_1 + v_2$	25·7	31·9	43·2	**Rb** r_1 = 1·48 v_1 = 13·6	$v_1 + v_2$	38·4	44·6	55·9
	Δv	28·9	39·5	57·4		Δv	52·3	62·7	81·6
$\Delta v/(v_1 - v_2)$ for 1 %		1·12	1·24	1·32	$\Delta v/(v_1 + v_2)$ for 1 %		1·36	1·40	1·46
, ,, 20 ,,		1·30	1·34	1·38	,, ,, 20 ,,		1·48	1·51	1·52
Na r_1 = 0·95 v_1 = 3·59	$v_1 + v_2$	28·4	34·6	45·9	**Cs** r_1 = 1·69 v_1 = 20·2	$v_1 + v_2$	45·0	51·2	62·5
	Δv	27·8	37·8	56·4		Δv	63·8	74·4	92·5
$\Delta v/(v_1 + v_2)$ for 1 %		0·976	1·09	1·22	$\Delta v/(v_1 + v_2)$ for 1 %		1·42	1·45	1·48
,, ,, 20 ,,		1·19	1·22	1·30	,, ,, 20 ,,		1·52	1·54	1·56
K r_1 = 1·33 v_1 = 9·86	$v_1 + v_2$	34·7	40·9	52·2	r_1 and r_2, Pauling ionic radii in Å.u., alkalis and halogens, respectively. v_1 and v_2, spherical volumes $\frac{4}{3}\pi r_1^3$, and $\frac{4}{3}\pi r_2^3$, respectively. Δv, apparent volume in (Å.u.)^3 of a pair of ions.				
	Δv	44·0	55·0	73·2					
$\Delta v/(v_1 + v_2)$ for 1 %		1·27	1·34	1·40					
,, ,, 20 ,,		1·44	1·46	1·48					

on the water structure involves an increase in density, and vice versa. This is not at once entirely harmonised with the view of Bernal and Fowler [11] that the addition of ion pairs gives a rise in "structural temperature," for this rise implies a decreased density. This point will require further consideration.

The conclusions of Table II. are suggestively significant. That they are somewhat tentative is illustrated by a change in calculations. If Pauling's ionic radii be used the results are as shown in Table III. It will be observed that while the conclusions are essentially the same, they are not quite so striking. The general view of the structure of the electrolyte remains.

The current discussions [17] concerning "order" and "disorder" in solid alloys evidently have a definite bearing upon liquids. When two liquids form a homogeneous solution there is a single common liquid structure, but with an unknown "degree of order". The phenomenon of solution, whether electrolytic or non-electrolytic, is concerned with forces that produce structure and that have a tendency to produce "order" corresponding to a super-lattice. But in a liquid the effect of temperature, on account of fluidity, would be quantitatively different. Thus the details of the theory will not be the same for the solid alloys and liquids, but probably there will be a strong similarity. The super-lattice found for ions has its correspondence in the alloy super-lattice. Even though the chief influence upon "order" in alloys may be eventually proved to be the interaction of neighbouring atoms, the "order" itself is extensive. It is in the corresponding effect in ionic solutions that is to be found the cause of the variation with concentration of the apparent volume of a pair of ions.

[17] Bragg and Williams, *Proc. Roy. Soc.*, 1934, **145**, 699, and 1935, **151**, 540; Williams, *Proc. Roy. Soc.*, 1935, 152, 231, Bethe, *Proc. Roy. Soc.*, 1935, **150**, 552; Peierls, *Proc. Roy. Soc.*, 1936, **154**, 207.

A few remarks concerning the present views of "liquid structure," may make the present status more clear. The literature of the subject does not so much indicate a wide or essential difference of concepts as to the nature of liquid structure as it does show in each contributed paper a view expressed in terms of the avenue of approach. To determine whether the liquid structure is an approximation to this or to that crystal structure, it is mathematically more feasible to assume a space arrangement or net-work around any (and every) scattering unit, but smoothed out with increasing distance not merely by temperature but also by fluidity. But it is also justifiable to accept the basic theory of diffraction from a crystal and to regard the melting as an alteration in stability of equilibrium introducing mobility. There are thus changes in density and in the resulting structure with a varying approximation of or approach to that of the crystal. Hence it is justifiable as a crude approximation to use Bragg's Law to determine the separation of equivalent "planes" of concentration of scattering centres. Here the crudeness of the approximation is at once apparent, though some have thought there is too definite a concept of structure when Bragg's Law is used.

Both of the above lines of approach are useful. Both involve very crude approximations. Both accept a semi-orderly arrangement of the scattering centres. The difference, if any, between authors pursuing one or the other lines of approach is in their detailed visualisation, which is not an essential feature.

To avoid the word "crystal" or "crystalline" in referring to the liquid, the author proposed the words "cybotaxis" and "cybotactic," believing that future discussion would profit by adopting a unique term for the liquid structure. If one takes an instantaneous view of the liquid, he does not see each point having a surrounding distribution of atoms, ions or molecules just like any other point, but he visions a decidedly spotted effect, there being regions of striking regularity and regions where at the moment regularity is difficult to recognise. Thus one is justified in using the word "group" to indicate the former, but again with no sharp boundaries or permanent association in mind. These spots or groups with undetermined size, shape, and time of duration can be given physical reality, but, unfortunately, instantaneous conditions cannot be measured.

The purpose of these remarks is to call attention to the rather crude approximations made by everyone attempting to describe liquid structure or cybotaxis. One may make quantitative determinations of the radial density distribution about any point by adopting the approximation first mentioned. On the other hand, the value of the instantaneous picture of inhomogeneity mentioned, while not so quantitative, has aided materially in the study of the subject. The above differences of concepts have assisted in progress but are otherwise of no moment. The present problem in the large now is to ascertain the significance of liquid structure in physics, chemistry, and biology.

Summary.

This paper emphasises the following interpretations of the already known facts concerning the alkali halides and their aqueous solutions :

(1) The almost constant density relationship between solid and liquid states for the halides of any one alkali point to a carry-over from solid to liquid of some structural effect produced by crystal forming forces.

(2) The melting-point and likewise the boiling-point depend directly and indirectly upon the forces which are responsible for the crystalline and liquid states. The fact that, with the alkali halides, certain melting and boiling-point anomalies are strikingly similar, indicates strongly, (*a*) that at least certain effects of these forces are characteristic of the alkali, and (*b*) that these characteristics are carried over from the solid to the boiling-point. This makes reasonable also characteristic structural differences in the liquid state.

(3) The data concerning the apparent volume of these halides in a water solution are in harmony with the following interpretation, (1) that, in addition to hydration of Li^+ and Na^+, the ions affect the semi-orderly structure of the water at distances much larger than the ionic radii, and (2) that this structural effect is responsible for the variation with concentration of the apparent volume occupied by a pair of ions, (3) that the structural effect, while characteristic of the halide, depends more upon the alkali than the halogen. These interpretations have not yet reached a quantitative stage (and are not thereby unique) and obviously cannot be applied to all the known facts of ionic solutions. They are herein emphasised because of their value in concepts and in experimental suggestions.

ELECTRICAL FORCES BETWEEN IONS AND NEUTRAL MOLECULES IN AQUEOUS SOLUTION. A STUDY OF THE "SALTING-OUT" EFFECT.

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In general the behaviour of solutions containing ions may be described by either a chemical or a physical method. Chemical discussions of such systems have been less popular in recent years because they make extensive use of such terms as association and solvation which cannot be given quantitative definition. The physical interpretations are sometimes criticised because certain of the simplifications introduced to avoid mathematical and other complications are difficult to justify, yet they have met with remarkable success and it seems proper to remark that the simple physical picture comes close to an adequate and quantitative account. In the physical theories the ion is considered as an electrical charge superimposed upon a neutral molecule, with this unit acting like other molecules except that its behaviour is modified by the fact of the charge. In a mixture of non-electrolytes, deviations from the laws of ideal solutions are practically always present and of course the forces which cause these deviations persist when electrolytes are added. When the ions are introduced other forces come into existence among which are those causing the salting-out or the salting-in of neutral molecules. This interaction of electrolytes and non-electrolytes has been the subject of theoretical study by Butler, Debye, Scatchard, and others.

The change in the solubility of a non-electrolyte in water caused by the addition of an electrolyte has been investigated over a long period of years. Various empirical equations have been used to describe these solubility relationships and at least one of them, that proposed as early as 1875 by Setschenow, has been quite successful in its description of the results of experiment even when the concentrations of salt used were as high as two and three in molarity. Perhaps too much thought has been devoted to the concentration and nature of the added electrolyte because one finds in the extensive literature of the subject many statements to the effect that changes in solubility are not influenced greatly by the character of the non-electrolyte. The incorrectness of this point of view has been recognised in the more recent physical and mathematical descriptions of the process, according to which an electrical charge attracts a medium of high dielectric constant or electrical susceptibility in the same way that a magnet attracts material of high magnetic susceptibility. Since the dielectric constant of water is more frequently higher than that of other neutral molecules it usually happens that water is preferentially pulled into the field existing about the ions. In such cases the less polar non-electrolyte molecules are forced into the portions of the solution remote from the field of the ions, there is an increase of the non-electrolyte to water ratio in those regions of the solution containing the non-electrolyte, and there results a reduction of the solubility of the non-electrolyte, referred to the total water present. If the dielectric constant of the non-electrolyte is higher than that of water it will concentrate in the region of the ions at the expense of the water, the non-electrolyte to water ratio in regions removed from the ions is lowered, and water is available to take up more of the neutral molecules.

The two Debye theories [1] consider the ions as rigid spheres with the neutral molecules behaving as a continuous medium whose interaction with the ions is determined by the macroscopic dielectric constant. The first theory is inexact in that it expresses, by the familiar Born method, the free energy of the solution in terms of the reversible work of transfer of the ions from water to the solution without recognition of the effect of these ions in producing a non-uniform distribution of the non-electrolytes present. The improvement in the second theory is a result of the successful expression of the change of concentration of the non-electrolyte solute with changing distance from the ion. The importance of this achievement has been suggested by the qualitative statements made in the previous paragraph.

The quantitative expression for the concentration in mole fraction of neutral molecules m_2 at any point of distance r from the centre of an ion is $m_2 = m_2^0 \exp\left(-\frac{\bar{R}^4}{r^4}\right)$, where m_2^0 is the concentration at infinite tance and $\bar{R}$ is a characteristic length. The evaluation of the characteristic length involves certain universal and molecular constants and dielectric constant data for the aqueous non-electrolyte solutions. It is convenient for the present to express the final result of the Debye calculations in terms of the activity coefficient of the non-electrolyte f_2 in an aqueous salt solution by the equation

$$\frac{1}{f_2} = 1 - \frac{4\pi N}{1000}\Sigma C_i I_i \quad . \quad . \quad . \quad . \quad (1)$$

Here
$$I_{i_{(1)}} = \int_{a_i}^{\infty}(1 - e^{-\bar{R}^4/r^4})r^2 dr, \text{ when } D = D_1(1 - \alpha C_2) \quad . \quad (2)$$

and
$$I_{i_{(2)}} = \int_{a_i}^{\infty}(1 - e^{+\bar{R}^4/r^4})r^2 dr, \text{ when } D = D_1(1 + \alpha C_2) \quad . \quad (3)$$

[1] (*a*) Debye and McAulay, *Physik. Z.*, 1925, **26**, 22; (*b*) Debye, *Z. physik. Chem.*, 1927, **130**, 56.

The characteristic length is calculated to have the value,

$$\bar{R}^4 = \alpha\frac{z_i^2 e^2 10^3}{8\pi RTD^0} = \frac{z_i^2 e^2 V_1}{8\pi RT}\cdot\frac{D_1 - D^0}{D^0 D_1 m_2^0} \quad . \quad . \quad . \quad (4)$$

The symbols used are largely familiar; D^0 is the dielectric constant of the saturated non-electrolyte solution, D_1 is that of the solvent, in this case water, a is a radius, V_1 is the molar volume of water, C_2 is the concentration of non-electrolyte in moles per litre, and the subscripts i designate properties and concentrations of ions.

The integral I_i can be expanded for evaluation as either of the following two series,

$$I_{i(1)} = \bar{R}^3\left[1{\cdot}21 - \frac{1}{3}\left(\frac{a}{\bar{R}}\right)^3 - \dots\right](\bar{R} > a) \quad . \quad . \quad (2a)$$

$$I_{i(1)} = \frac{\bar{R}^4}{a}\left[1 - \frac{1}{2!\,5}\left(\frac{\bar{R}}{a}\right)^4 + \dots\right](\bar{R} < a) \quad . \quad . \quad (2b)$$

If the dielectric constant of the solution is greater than that of the water and if the radius a is larger than $\bar{R}$ we make use of the series,

$$I_{i(2)} = \frac{\bar{R}^4}{a}\left[1 + \frac{1}{2!\,5}\left(\frac{\bar{R}}{a}\right)^4 + \dots\right](\bar{R} < a) \quad . \quad . \quad (3a)$$

When the ions in question become very small it is sufficient for our present purpose to remember that strong salting-in must result and there will be interactions because of the geometrical configurations of ion and neutral molecule not accounted for by the theory.

The equations presented above have been derived from the final distribution equation which applies in the case of a mixture containing only small quantities of the neutral molecule. The more general distribution equation is

$$v_2 \ln\frac{m_1}{m_1^0} - v_1 \ln\frac{m_2}{m_2^0} = \frac{e^2 z_i^2}{8\pi kT}\cdot\frac{1}{D^2}\left(v_2\frac{\partial D}{\partial n_1} - v_1\frac{\partial D}{\partial n_2}\right)\frac{1}{r^4} \quad . \quad (5)$$

Here, the quantities n_1 and n_2 are numbers of molecules per cubic centimeter, v_1 and v_2 are the volumes of single solvent and solute molecules, and m_1 and m_2 are the mole fractions of components 1 and 2, in our case water and non-electrolyte, respectively. Thus, if we know the dielectric constant D of a solution as a function of the composition of the mixture we can calculate the concentration of both components at any distance r from the ion. Phenomena of electrical saturation in the neighbourhood of the ion have been neglected. In general, equation (5) ought to be used. In this way the total effect of the ion is obtained from the curve of concentration as a function of r by integration over the whole of the space surrounding the ion. We have found it convenient to perform this integration by a graphical method.

In the concluding sentence of the article in question, Debye remarks that in order to judge of the value of his theory accurate solubility (salting-out) data will have to be used in combination with almost non-existent dielectric constant measurements. From the mathematical expressions written down, it is seen that for this purpose observations must be made of the change of dielectric constant of the solution with concentration of non-electrolyte or of the dielectric constant of the saturated non-electrolyte solution. Now, nearly ten years later, such information is available in comparatively few instances even where more or less adequate solubility data are to be found. Dielectric constant measurements such as are to be reported here have been made in the attempt to contribute toward seeing whether or not this consideration of the ions as rigid spheres and the non-electrolyte solution as medium whose interaction with the ions is determined by the ordinary dielectric constant does adequately explain the salting-out effect in the limiting case of vanishingly small electrolyte concentration. It can be shown without difficulty that in solutions of somewhat higher electrolyte concentration there will be a distinct weakening of the electrical field due to the mutual interaction of the ions. In other words, the mathematical expressions given above are limiting laws and are to be considered as such.

Previous Work.

Foremost among the previous attempts at verification of the improved Debye theory may be mentioned the determinations by Gross and associates,[2] of the change of the partition of acetone and of hydrocyanic acid between benzene and water caused by the addition of salts of several valence types to the water. In qualitative agreement with the predictions of the theory, acetone is salted out of water, and, except in a few cases (*e.g.* lithium nitrate, and magnesium chloride), hydrocyanic acid exhibits the anticipated inversion due to its higher dielectric constant. In amount the effect observed with the two non-electrolytes agrees approximately with the requirements of the theory for a number of nitrates, chlorides and sulphates, and these effects are of approximately the same magnitude when referred to the same ionic strength. In general the differences between the requirements of the theory and the results of salting-out measurements become smaller and smaller as the electrolyte concentration is reduced. These differences are due in part to the fact that the measurements were made in a concentration range too high for the limiting law of the theory and in part to inaccuracies in the dielectric constant data which had to be used in the calculations.

In an article which has just made its appearance, Scatchard and Benedict[3] have presented precision data for the freezing-points of aqueous solutions of mixtures of each of the chlorides of lithium, sodium, and potassium with dioxane. The freezing-point depressions are expressed as the osmotic coefficient for the chemical potential of the solvent at the freezing-point of the solution. At low salt concentrations the observed osmotic coefficients of the mixtures agree so well with the requirements of the theory in question that the small differences might easily be accounted for by errors in the atomic radii by inexactnesses introduced through the simplifying assumptions of the theory or by slight inaccuracies in the freezing-point data. The dielectric constant data for the aqueous dioxane solutions required in the comparison were obtained especially for the purpose by Wyman.

Evaluation of Theoretical Solubility.

In the reports of work in which the Debye theory has been investigated it has been customary to use equation (4) in order to determine the characteristic length. We have preferred to use in our calculation a somewhat more exact equation,

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[2] Gross and associates (Schwarz and Iser), *Sitz. Ber. Akad. Wiss. Wien*, (11*b*), 1930, 139, 179, 221 ; *Monatsh. Chem.*, 1930, 55, 287, 329. Gross, *Acta Physicochimica*, 1935, 3, 583. See also Falkenhagen, *Elektrolyte*, Hirzel, Leipzig, 1932.

[3] Scatchard and Benedict, *J. Am. Chem. Soc.*, 1936, 58, 837.

$$\bar{R}^4 = \frac{z_i^2 e^2}{8\pi RT} \cdot \frac{D_1 - D^0}{D_1 D^0} \cdot \frac{M_1 d_2 m_1^0 + M_2 d_1 m_2^0}{d_1 d_2 m_2^0} \quad . \quad . \quad (6)$$

in which it has been assumed the density of the system obeys the ideal solution law. In the equation M_1 and M_2 are molecular weights and d_1 and d_2 are densities of water and non-electrolyte, respectively.

It would have been even more exact to have used a longer semi-graphical method we have developed, but, because of lack of exactness in available solubility measurements and because of the influence of factors which have not as yet been taken into account in the theory, comparatively few computations have been made with it. Our equation (5) may be written in the form,

$$2{\cdot}3\, v_1\left\{\frac{v_2}{v_1}\log(1 - m_2) + \log m_2^0 - \log m_2 - \frac{v_2}{v_1}\log m_1^0\right\} = \frac{z_i^2 e^2 (D_1 - D^0)(v_1 + [v_2 - v_1]m_2)^2}{8\pi kTD^2 m_2^0 r^4} \quad (7)$$

in which v_1 and v_2 are the volumes in cubic centimeters of a single molecule of solvent and solute, respectively. The assumption is made here that for the smaller concentrations the dielectric constant is a linear function of concentration. Thus, the dielectric constant, D, of such a solution containing water and non-electrolyte is made up of two constituent parts such that,

$$D = D_1 m_1 + D_2 m_2,$$

and

$$D_1 - D_2 = \frac{D_1 - D^0}{m_2^0}.$$

Since $\left(\frac{e^2}{2{\cdot}3 \times 8\pi k}\right)^{\frac{1}{4}} = 0{\cdot}0732$, we have, in solving for r,

$$r = 0{\cdot}0732\left(\frac{z_i^2(D_1 - D^0)}{v_1 m_2^0 T}\right)^{\frac{1}{4}} \left[\frac{\{v_1 + (v_2 - v_1)m_2\}^{\frac{1}{2}}}{\left\{\frac{v_2}{v_1}\log(1 - m_2) - \log m_2 + \log m_2^0 - \frac{v_2}{v_1}\log m_1^0\right\}^{\frac{1}{4}} D^{\frac{1}{2}}}\right] \quad (10)$$

Inasmuch as the factor in parentheses will be constant for any given system, this equation gives r as a function of m_2 and D. The dielectric constant for the solution at any concentration m_2 is obtained from the experimental observations. Instead of making use of a curve r, plotted as a function of m_2, we prefer to represent the distance as a function of the amount salted out per cubic centimeter in moles multiplied by $4\pi r^2$. Thus the area under such a curve will measure the number of moles of non-electrolyte salted out per ion. If the number of moles of non-electrolyte per cubic centimeter in a saturated solution in water is h^0, and h is the corresponding quantity at such a distance from the ion that the concentration of non-electrolyte is m_2, then

$$h^0 - h = d_1 d_2\left[\frac{m_2^0}{M_1 d_2 - m_2^0(M_1 d_2 - M_2 d_1)} - \frac{m_2}{M_1 d_2 - m_2(M_1 d_2 - M_2 d_1)}\right] \quad (11)$$

$$= d_1 d_2\left[\frac{M_1 d_2 (m_2^0 - m_2)}{\{M_1 d_2 - m_2^0(M_1 d_2 - M_2 d_1)\}\{M_1 d_2 - m_2(M_1 d_2 - M_2 d_1)\}}\right] \quad (12)$$

The evaluation of the amount of non-electrolyte salted out is best demonstrated by the application of our method to a specific example For this illustration we choose the system ethyl ether-water-electrolyte. The actual data adopted are exactly those used by Debye in the original article 1*b*, for in this way we obtain direct comparison with his result The main portion of the amount of non-electrolyte, in this case ethyl ether, salted out is obtained by a graphical integration The number of moles salted out per ion is $\int 4\pi r^2(h^0 - h)dr$. Now, if the factor in brackets of equation (10) is set equal to $W \times 10^{-12}$ and other numerical data are introduced, the equation becomes $r = 3{\cdot}325 \times 10^{-8}\, W$.

Also,
$$h^0 - h = \frac{0{\cdot}660\,\Delta}{12{\cdot}77 + 61{\cdot}23\, m_2} = \frac{0{\cdot}660\,\Delta}{13{\cdot}72 - 61{\cdot}23\,\Delta} \quad . \quad (13)$$

where $\Delta = m_2{}^0 - m_2$. Therefore,

$$\int 4\pi r^2(h^0 - h)dr = 0{\cdot}305 \times 10^{-26}$$
$$\times \left[\text{Area under curve when } \frac{W^2 \,.\, \Delta \,.\, 10^5}{12{\cdot}77 + 61{\cdot}23\, m_2} \text{ is plotted against } W\right] \quad (14)$$

The plot actually used is reproduced to form Fig. 1. In the example presented here we have determined with planimeter the area under the curve out to the point where r is large enough so that $\Delta = 0{\cdot}0001$. Thus, after allowance for the volume actually occupied by the ion itself, we find

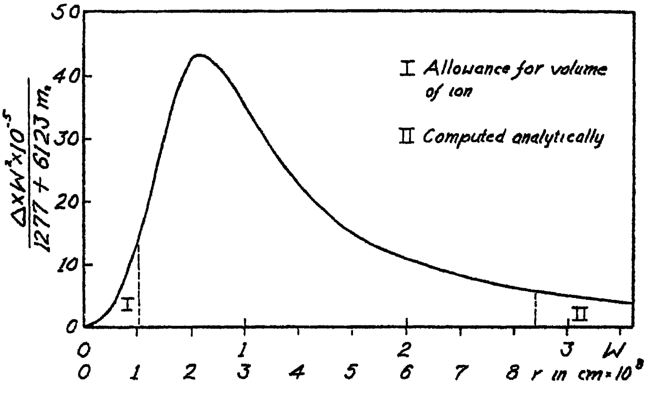

FIG. 1.—Curve for Evaluation of Theoretical Amount of Salting-Out by Semi-Graphical Method.

$$\int 4\pi r^2(h^0 - h)dr = 14{\cdot}93 \times 10^{-26} \text{ mole} \quad . \quad . \quad (15)$$

An analytical method is used to determine the area under the curve from a point where r is large enough so that $\Delta = 0{\cdot}0001$ and r has value $r = r_\Delta$, out to $r = \infty$ where Δ becomes zero. For such small values of Δ, $h^0 - h = 0{\cdot}0481\,\Delta$, and

$$\frac{v_2}{v_1} \ln (1 - m_2) - \ln m_2 + \ln m_2{}^0 - \frac{v_2}{v_1} \ln m_1{}^0 = \Delta \left\{ \frac{v_1 + (v_2 - v_1)m_2{}^0}{v_1 m_2(1 - m_2{}^0)} \right\} \quad (16)$$

Thus, the relation between r and m_2 now becomes,

$$r = 4{\cdot}09 \times 10^4 \left[\frac{\{v_1 + (v_2 - v_1)m_2{}^0\}^{\frac{1}{2}}}{\left\{\Delta\left(\frac{v_1 + (v_2 - v_1)m_2{}^0}{v_1 m_2{}^0(1 - m_2{}^0)}\right)\right\}^{\frac{1}{2}} D^{\frac{1}{2}}} \right] \quad (17)$$

Substituting the proper numerical data, we have

$$r = \frac{0{\cdot}923 \times 10^{-8}}{\Delta^{\frac{1}{2}}} \quad . \quad . \quad . \quad . \quad (18)$$

The amount of non-electrolyte salted out per ion under these conditions is

$$\int_{\infty}^{r_\Delta} 4\pi r^2(h^0 - h)\mathrm{d}r = 4{\cdot}76 \times 10^{-26} \text{ mole} \quad . \quad . \quad (19)$$

The total amount of ether salted out per ion is now $(14{\cdot}93 + 4{\cdot}76)$ $10^{-26} = 19{\cdot}69 \times 10^{-26}$ mole. In a normal solution of uniunivalent strong electrolyte there are $12{\cdot}1 \times 10^{20}$ ions per cubic centimeter and the total amount of ether salted out is 238×10^{-6} mole. The amount present per cubic centimeter in the absence of electrolyte is,

$$h^0 = \frac{m_2{}^0 d_1 d_2}{M_1 m_1{}^0 d_2 + M_2 m_2{}^0 d_1} = 801 \times 10^{-6} \text{ mole.} \quad . \quad (20)$$

Therefore the per cent. of ether salted out is 29·7 per cent. The original Debye figure is 28·5 per cent.

Experimental Results.

We proceed now to make a comparison of the requirements of the more exact salting-out theory of Debye with certain data at several temperatures for the solubility of ethyl acetate in aqueous salt solutions now existent in the literature. For this comparison it has been necessary to make precision determinations of the dielectric constant of aqueous ethyl acetate solutions at the temperatures 25°, 28° and 50° C. The method was one of substitution used in connection with a radio-frequency bridge of conventional design.[4] The source of alternating current, coupled inductively to the bridge, was an oscillator of the Hartley type modulated with a 1000 cycle microphone hummer. Inductance and capacitance were adjusted to give to the carrier wave the frequency $0{\cdot}57 \times 10^6$ cycles. The detector was a commercial radio receiver, powered throughout with direct current. It was found convenient to use a dielectric cell which is arranged so that capacity measurements were made with a variable condenser. Dielectric constant values were obtained by dividing the difference in capacity between two fixed positions when the plates were immersed in the solution by the difference in capacity between the same positions with air as dielectric. The dielectric cell was designed and constructed to give proper shielding, rapid heat exchange with thermostat bath, low capacitative and inductance effects between leads, and exactness in operation.

Throughout the course of the experimental work every effort was made to obtain results of high precision. The solvent used was in every case a water having a specific conductance not greater than 1×10^{-6} mhos. The ethyl acetate obtained from the Eastman Kodak laboratories was treated for the removal of free acid and alcohol, dehydrated and subjected to a series of fractionations until consistent boiling specimens were obtained. The densities at the several temperatures and the boiling-point of the fractions used were always consistent with corresponding figures given by Wade and Merriman [5] and by Mathews.[6] The solutions were made up by a weight method which eliminated as far as possible error due to the volatility of the ester.

Glasstone and Pound [7] have recorded data for the change in solubility of ethyl acetate in aqueous solutions containing electrolytes of 1-1 valence type. The solubility determinations were made in such a way as to show the effect of increasing electrolyte concentration at the temperatures 25° and 50° C. The dielectric constant data for the system ethyl acetate-water obtained by us were found to be linear in concentration of ethyl acetate measured in per cent. by weight and the experimental results at these temperatures can be expressed in terms of first degree equations involving the dielectric constant of water and the slope of the dielectric constant—per cent. by weight of ethyl acetate, p, curve, as follows,

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[4] Daniels, Mathews, and Williams, *Experimental Physical Chemistry*, 2nd ed., McGraw-Hill Book Co., New York, 1934.

[5] Wade and Merriman, *J. Chem. Soc.*, 1912, **101**, 2429.

[6] Mathews, *J. Am. Chem. Soc.*, 1926, **48**, 562.

[7] Glasstone and Pound, *J. Chem. Soc.*, 1925, **127**, 2660.

$$D_{25} = 78{\cdot}48 - 0{\cdot}767\,p.$$
$$D_{50} = 69{\cdot}95 - 0{\cdot}641\,p.$$

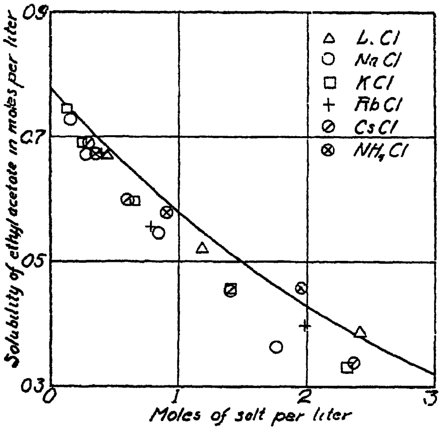

FIG. 2.—Observed (Glasstone and Pound) and Calculated Solubilities of Ethyl Acetate in Aqueous Solutions Containing Chloride Salts at 25° C.

The solubility data of Euler[8] for the system ethyl acetate-water-electrolyte were obtained at 28° C. In order to make use of these data we have determined the dielectric constants of water and a saturated solution of ethyl acetate in water at this temperature, with results $D_1 = 77{\cdot}41$ and $D^0 = 71{\cdot}80$. The limiting slopes at the several temperatures for the solubility of ethyl acetate as a function of salt concentration have been calculated by using equation (6). In regions of higher electrolyte content, these solubilities either can be represented by extrapolation of the line of limiting slope or they may be approximated with the use of additional theory or guiding principle. We have adopted the second course and have constructed an empirical curve by using the Setschenow equation with its constant so evaluated as to give the theoretical limiting slope. As Fig. 1 indicates, this equation leads to a result of the type to be expected by the theory when the ions are crowded more closely together. The results of the calculations may be expressed by relatively simple equations, as follows:

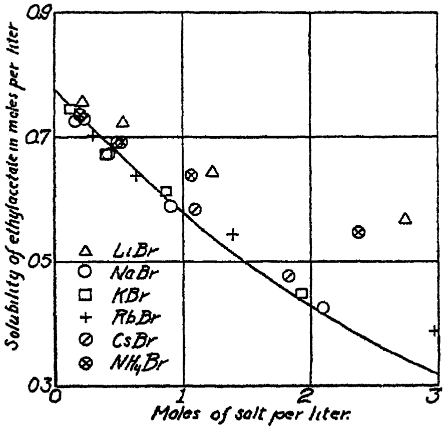

FIG. 3.—Observed (Glasstone and Pound) and Calculated Solubilities of Ethyl Acetate in Aqueous Solutions Containing Bromide Salts at 25° C.

At 25° C., $\log C_2 = 0{\cdot}108 - 0{\cdot}130\,C_s$

At 50° C., $\log C_2 = 0{\cdot}195 - 0{\cdot}127\,C_s$

These equations are applicable to systems containing salts of the 1-1 valence type when the concentrations of non-electrolyte and salt are expressed in moles per litre. The comparison of calculated and experimental solubilities at 25° is shown in graphical form by means of Figs. 2, 3 and 4 in which the solubility of ethyl acetate is given as a function of electrolyte concentration for chloride, bromide, and iodide salts. The full line in each of the figures gives the calculated solubility. The data and curves for the solubilities at 50° are similar in every respect. Fig. 5 has been constructed from the experimental solubility data of Euler at 28° C. and from the calculated solubilities which were obtained by using the dielectric constant data given above to give the limiting slope of the full lines which give the calculated solubilities, this time in the presence of electrolytes of valence type 1-1, 2-1 and 2-2.

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[8] Euler, *Z. physik. Chem.*, 1899, 31, 360.

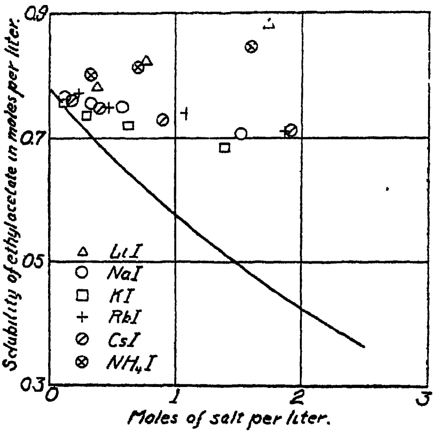

FIG. 4.—Observed (Glasstone and Pound) and Calculated Solubilities of Ethyl Acetate in Aqueous Solutions Containing Iodide Salts at 25° C.

Limitation of space makes it impossible to include at this time additional dielectric constant data which have been obtained for aqueous solutions of acetone, aniline and ethyl ether at several temperatures and the results of numerous calculations made from them. Also, Mr. R. W. Wright,[9] working with one of us (P. S. A.) has obtained similar data for comparison with the solubilities of phenylthiourea in ethyl alcoholic electrolyte solutions reported by Thorin.[10] These data will be presented elsewhere.

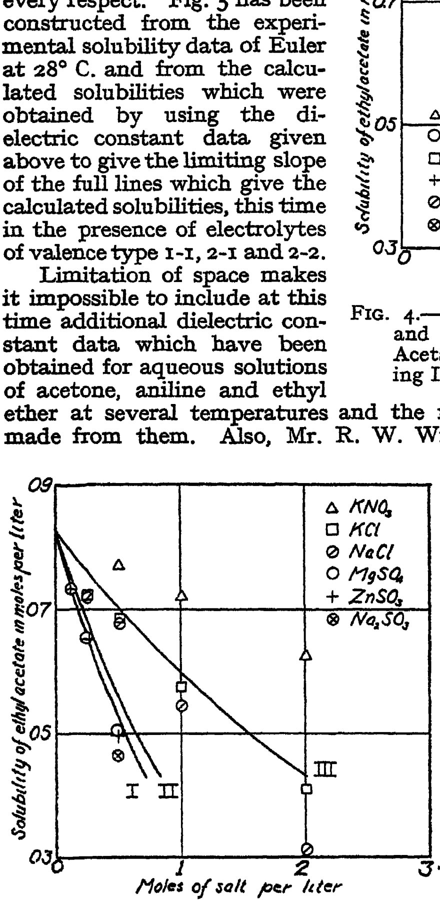

FIG. 5.—Observed (Euler) and Calculated Solubilities of Ethyl Acetate in Aqueous Solutions containing Electrolytes of Several Valence Types at 28° C.

Curve I—Valence Type 2-2.
Curve II—Valence Type 1-2.
Curve III—Valence Type 1-1.

Conclusions.

Since the publication in 1927 of the Debye theory describing the salting-out effect, the attempts to test its validity have been few in number and limited in extent. It has been and is the most important object of our work to undertake a more systematic study of the problem than has been attempted to date by providing suitable precision dielectric constant data for the calculation of the theoretical solubilities in a number of instances where the results of reliable solubility determinations are available. The data for the ethyl acetate solubilities given in graphical form above are representative of our data in every way so that we consider conclusions drawn from them to be quite general in character.

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[9] Wright, *B.A. Thesis, Southwestern College, Winfield, Kansas*, 1936.
[10] Thorin, *Z. physik. Chem.*, 1915, 89, 685.

In the majority of cases in the very dilute salt solutions, the results of the dielectric constant measurements lead to calculated solubilities in good agreement with those actually observed. In the cases of systems containing moderate to high concentrations of electrolyte, the comparison of the actual amount of salting-out with that demanded by the theory indicates that in some cases a displacement of the non-electrolyte from the space surrounding an ion by the electrical field plays a major rôle while in others it appears to be of lesser consequence. In these latter cases ion hydration may act to cause an abnormally high salting-out and aggregation of non-electrolyte molecules, especially about the anions, results in a lowered salting-out or even a salting-in. The reason for such an aggregation of non-electrolyte about a spherical ion like the iodide ion is difficult to understand but the effect is sometimes pronounced. In such cases in general the geometrical configuration of ion and neutral molecule will be decisive because of the possibilities for segregation and orientation inherent in such a situation. From the calculations, it is evident the theory requires the concentration of a non-electrolyte of lower electrical susceptibility in the near vicinity of the ion to be practically zero which in the cases investigated by us is equivalent to saying the ion is hydrophilic. Thus, hydration in excess of this amount will be required to cause an abnormally high salting-out effect. Actually, excess salting-out is not common and it may be that with more accurate solubility data it will be found to be even less prevalent than now appears.

It is our desire to call attention in this report to the fact that the dielectric constant measurements lead to calculated solubilities in good or excellent agreement with those actually observed in the more dilute salt solutions and when differences appear they seem to be due to the fact that the measurements were made in a salt concentration range too high for the limiting law of the theory. This agreement, together with a study of the deviations as the electrolyte content is increased, should give cause for considerable confidence in the essential correctness of the basic assumptions upon which the theory is based and give encouragement to further research to discover the exact nature of the additional factors which contribute to the salting-out and salting-in at the higher salt concentrations.

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THE REFRACTOMETRIC CURVES AND THE STATE OF DISSOLVED STRONG ELECTROLYTES.

By A. E. Brodskii.

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The state of strong electrolytes in solutions is still one of the important unsolved problems of physical chemistry. Association increasing with concentration has an influence upon the conductivity and the thermodynamical properties of electrolyte solutions in the same direction as the increasing interaction of the ion fields when they draw together. So far, neither effect has been discovered by the experimental methods of classical electrochemistry, and the future value of these methods in solving this problem is doubtful. On the other hand, recent new methods of investigation (electro-conductivity in strong and high-frequency fields, X-ray and electron diffraction, the refraction and scattering of light, etc.) have proved fruitful, although they have not yet given unambiguous results in any case, owing both to the insufficient treatment of the theory and to the limited experimental resources. The incompleteness of the theory is particularly revealed in connection with deformation phenomena. It appears that considerable success in this direction may be expected only from the use of quantum mechanics.

The Sutherland-Bjerrum hypothesis on the complete dissociation of strong electrolytes in solutions of any concentration could be confirmed only by indirect data; some of them are fairly convincing, but so far no *experimenti crucis* has been found for this hypothesis. We can speak only of the degree of its probability, as to which the opinions of different electrochemical schools differ greatly.[1]

Each of the methods serving to solve the problem is, therefore, worth careful study and criticism. The particularly complex question of the deformation phenomena in a solution may be studied successfully from the curves of the apparent refractivity of dissolved substances. Fajans and his co-workers [2] used the deviation from additivity of the refractivity of solutions for their conclusions as to the state of dissolved electrolytes, but in comparatively concentrated solutions (to which the initial study was limited) the matter is very complicated. It was necessary therefore to transfer the study into the realm of dilute solutions and to extend it to non-electrolytes in order to determine to what extent the observed peculiarities of the refractivity curves characterise strong electrolytes. The experimental part of this paper deals with our work on this subject.

Refractive Indices.

The study of the refraction of dilute solutions necessitated working out methods for the measurement with great precision of the difference Δn of refractive indices and the difference Δd of densities of the solution and solvent. The error contributed to the value of the apparent molar refractivity R of a dissolved substance by errors $\delta(\Delta n)$ and $\delta(\Delta d)$ of these difference measurements is approximately defined [3] by the expression:

$$\delta(R) = \frac{100}{c_v}[2\delta(\Delta n) + 6\delta(\Delta d)],$$

where c_v is concentration in mol./1. Thus, when c_v is of the order 10^{-1} to 10^{-2}, the values Δn and Δd have to be measured with precision of the order 10^{-6} to 10^{-7}. Neither a refractometer nor the usual picnometric measurements is suited for this purpose.

For the measurement of Δn of diluted solutions an interferometer was used. The author, with Shershever and Filippova,[4] secured the precision to 1 to 2 × 10^{-7} units for Δn in the concentration region from 0·001 molar to > 1 molar. For more concentrated solutions a refractometer must be preferred. The points obtained by both methods are easily placed on the same Π-curve, giving trustworthy results for the whole region from 0·001 molar to the most concentrated solutions. So far, measurements have been made in this way for solutions of KBr, KNO_3, NaCl,[5] TlCl, $TlNO_3$ [6] in dilutions down to 0·1 molar and KCl [7] and urea [8] throughout their concentration range.

The refractivity of a dissolved substance may be represented as the sum of two factors: $\Pi(c_v, \Delta n)$ and $\Phi(c_v, \Delta d)$, where

$$\Pi = \frac{1000}{c_v}(\rho - \rho_0),$$

and $\rho = \frac{n^2 - 1}{n^2 + 2}$ and $\rho_0 = \frac{n_0^2 - 1}{n_0^2 + 2}$, n and n_0 being the refractive indices of a solution and solvent. The figure shows the complete Π-curves for solutions of urea and potassium chloride in water, the data of another laboratory[9] for KCl and Dicova[10] and Shershever's measurements in my laboratory for urea by means of a refractometer, being used for concentrated solutions (over 1·1 molar). All measurements were made at 25° in the light of the yellow He-line.

When we started our measurements, interferometric measurements with a different way of finding shifts were also commenced at Fajans' laboratory.[11]

Molar Volumes.

An exact definition of Δd of diluted solutions presents considerable difficulties. We first tried to use the float method, proposed by Kohlrausch and Hallwachs,[12] but could not bring the precision of the measurements to 10^{-6}. Recently my co-workers Scarre and Demidenko[13] achieved the precision of 1×10^{-6} for Δd, by a variation of the method of Washburn and Smith,[14] whereby two identical 50 c.c. picnometers with calibrated capillary necks and arbitrary marks on them are filled to an arbitrary height, one (*A*) with water and the other (*B*) with solution. The heights above the marks are measured by a cathetometer to 0·005 mm. in a thermostat regulated to a temperature constancy of 0·002°. The weight difference of two picnometers can be ascertained to 0·00003 g. The operation is then repeated with the picnometer *A* filled with solution and the picnometer *B* filled with water. Δd is calculated from the height and weight differences.

The method was checked at first on potassium chloride. Four points between 0·1-0·01 molar coincided to 0·002 c.c. of the value of Φ, with the very precise measurements of Geffcken and Price.[15] Urea solutions were then measured in the concentration range from 0·0035 to 1·3 molar.

In the figure the Φ-curves are illustrated over a large concentration range for KCl and urea. Φ is equal to the apparent molar volume of a dissolved substance multiplied by ρ_0:

$$\Phi = \rho_0\left(\frac{M}{d_0} - \frac{1000}{c_v}\frac{\Delta d}{d_0}\right),$$

where M is the molecular weight, d_0 the water density, and $\rho_0 = 0{\cdot}20547$ for the yellow He-line at 25°. The curve for KCl is drawn from the data of Geffcken, etc. (l.c.) conforming as mentioned with our data. The curve showing Scarre and Demidenko's data for urea was completed from the usual picnometric measurements of Dicova[10] for more concentrated solutions (1·4 to 4·4 molar). The curves both for KCl and for urea show typical differences, to which we shall refer later.

The precision for Δd of 1×10^{-6} is insufficient for dilutions below 0·01 molar. Methods now being worked out, aiming at a precision of 1×10^{-7} units, will make it possible accurately to study refractivity curves to dilutions of the order 0·001 molar. A somewhat greater precision than ours (some units 10^{-7}) was reached by Geffcken, Beckmann and Kruis,[16] by means of rather complicated differential methods. In addition to the data for KCl we made use also of these authors' measurements for NaCl in combination with our Δn to get a refractivity curve of this electrolyte.[5]

The Comparison of Results for an Electrolyte and Non-Electrolyte.

To a first approximation we may take $R = \Phi + \Pi = \text{const.}$ Thus, to this approximation, Φ- and Π-curves are symmetrical with regard to the concentration axis, and we need only consider the Φ-curve, the theoretical explanation of which is simpler.

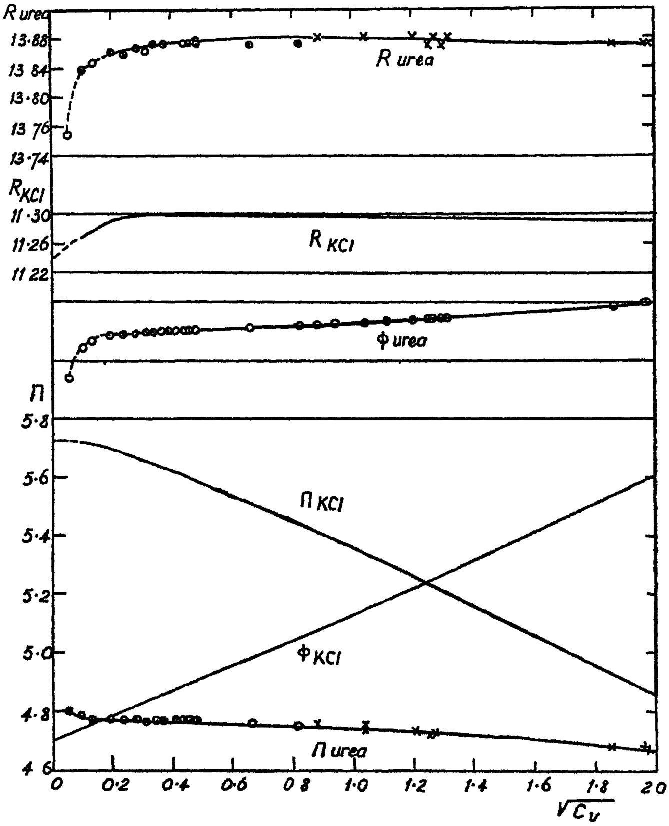

FIG. 1.

Φ-curves for a typical strong electrolyte (KCl) and a non-electrolyte (urea) illustrated in the figure as a function of $\sqrt{c_v}$, reveal a characteristic difference which recurs also in other examples which will be the subject of a later publication.

For a strong electrolyte dissociated completely the Debye and Hückel theory requires the Φ-curve to approximate asymptotically to the limiting straight line on increasing dilution :

$$\Phi = \Phi_0 + a\sqrt{c_v}$$

with $a = 0{\cdot}38$ for 1-1 electrolyte at 25° in water.[17] The Φ-curve for KCl completely satisfies this requirement; it is a straight line with $a = 0{\cdot}43$. A slight deviation from the theoretical value may be ascribed to the inaccuracy of the calculation.[18] We do not here consider the as yet unsolved problem, why the limiting law applies only to high concentrations.[19]

On the other hand, for urea, where interionic forces are absent, Φ is almost independent of concentration: from 0·04 to 1·45 molar Φ increases by 0·43 c.c. for KCl and only by 0·06 c.c. for urea. Below 0·04 molar for urea Φ decreases rapidly with concentration, but we cannot be sure that this decrease is not influenced by systematic errors.[20] Under all conditions below this concentration limit, the Φ-curve is not quantitatively reliable. In our measurements the precision of the Φ-curve is of the order $\frac{2 \times 10^{-7}}{c_v}$, giving an error of the order 0·005 c.c. for Φ when $c_v = 0{\cdot}04$ and 0·02 c.c. when $c_v = 0{\cdot}01$, and in this range the decrease of Φ is only 0·03 c.c.

The apparent molar refractivity curve of a dissolved substance is horizontal only to a first approximation. In fact, it reveals a distinct change of R with concentration. This change may be explained in different ways. Fajans concluded that the ion association of strong electrolytes increases with concentration to form non-dissociated molecules, a conclusion which is contrary to the present-day conception on complete dissociation of strong electrolytes. Again, we suggested the action of the ionic fields according to the Debye and Hückel theory, complicated in concentrated solutions by deformation phenomena, which, however, do not affect the association,[21] an explanation similar to that used for those authors for the Φ-curve. This led to some discussion,[22] to which we need not now refer.

The R-curves of a typical strong electrolyte and of a non-electrolyte (see also the figure) are very similar; hence we may conclude that the refraction curve does not lead to any direct conclusion as to the extent of dissociation of strong electrolytes in solution. In the light of these new data our previous explanation of the shape of the refractivity curves as influenced by the action of the ionic atmosphere fields also requires revision.

Unfortunately, we cannot yet give any authentic quantitative data as to the course of the urea R-curve in the interesting region of concentrations below 0·04 molar (see above), but the accelerated fate of the R-curve on approaching $c_v = 0$ is in this case as trustworthy as for electrolytes, which we first showed simultaneously with Geffcken.[9, 15] This fall renders doubtful the extrapolation to $c_v = 0$ previously made by other authors on the ground of rectilinear part of R-curve (above 1-2 molar), in order to obtain refractivity values of free dissolved ions.

The material on solution refraction is therefore at present insufficient for drawing conclusions as to the state of substances in solution. Measurements must be made with electrolytes and non-electrolytes in very dilute solutions, both in aqueous and in non-aqueous solvents. Such a study is being made in my laboratory.

The Influence of an Electrolyte upon the Refractivity of a Non-Electrolyte.

The change of an apparent molar volume with concentration must be ascribed not wholly and solely to the interaction of the ion fields on one another and to the solvent molecules. This is clear from the fact that a small change of Φ with concentration may be seen, even for a non-electrolyte, whose molecules also have a polarising effect. From this point of view it was interesting to ascertain to what degree an electrolyte influences the refraction of a non-electrolyte. For this purpose we studied a three-component system water-electrolyte-non-electrolyte. In the table results of Dicova are given for urea and potassium bromide solutions at different concentration ratios. R_u, R_B and R_0 denote molar refractivities of urea, and of KBr in water and of pure water, and R the molar refractivity of KBr + urea solutions of concentrations indicated (in mols. per 1000 g. of water). The value R is obtained from Δn, Δd and the average molecular weight of the solution, and the value R' is calculated on the assumption that the refractivity in the mixture is additive:

$$R' = \frac{R_u c_u + R_B c_B + R_0\, 1000/M_0}{C_u + C_B + 1000/M_0},$$

where M_0 is the molecular weight of water.

R_u', which is also given for urea in a mixture, was obtained by subtracting the refractivity of KBr (in the absence of urea) and of water from the refractivity R observed for the mixture.

THE ADDITIVITY OF THE REFRACTIVITY IN MIXTURES OF DISSOLVED UREA AND POTASIUM BROMIDE.

($t = 25°$, $\lambda = 5875{\cdot}6$Å, $R_0 = 3{\cdot}7121$.)

Solutions of Urea.		Solutions of KB$_r$.		Solutions of Urea + KB$_r$.				
c_u.	R_u.	c_B.	R_B.	R.	R'.	$R - R'$.	R_u'.	$R_u - R_u'$.
1·6842	$13{\cdot}87_9$	1·4335	$14{\cdot}88_3$	4·2778	4·2773	+ 0·0005	$13{\cdot}89_9$	$-\ 0{\cdot}02_0$
		2·2811	$14{\cdot}86_4$	4·4282	4·4279	+ 0·0003	$13{\cdot}89_1$	$-\ 0{\cdot}01_2$
		3·1099	$14{\cdot}84_5$	4·5708	4·5702	+ 0·0005	$13{\cdot}90_6$	$-\ 0{\cdot}02_7$
3·9265	$13{\cdot}87_1$	1·3337	$14{\cdot}88_8$	4·6137	4·6139	− 0·0002	$13{\cdot}87_1$	$0{\cdot}00_0$
		2·4515	$14{\cdot}86_0$	4·7977	4·7982	− 0·0005	$13{\cdot}86_3$	$+\ 0{\cdot}00_8$
		4·1082	$14{\cdot}82_1$	5·0574	5·0580	− 0·0006	$13{\cdot}86_4$	$+\ 0{\cdot}00_7$

From these data, the precision for R and R' is about 0·0003 c.c. and for R_B, R_u and R_u' is about $0{\cdot}03/c$. The differences $R - R'$ or $R_u - R_u'$ correspond approximately to the possible error. Thus, no marked mutual influence of the components upon one another is revealed in the mixture KBr + urea. It is possible that the lack of the influence of KBr-ions upon the urea refractivity is connected with the screening effect of surrounding dipoles of water on the fields of these ions.[23]

In two-component mixtures of two liquids, where this screening effect is absent, deformations to which dipole molecules are subjected are clearly manifest, *e.g.*, in Raman-spectra. Thus, we [24] have found that some frequencies of $AsCl_3$ are greatly shifted by the second component, if this has a considerable moment (methyl ethyl and *iso*-propyl alcohols) but not so in non-dipole liquids (CCl_4, C_6H_6). Phosphorus trichloride shows a similar effect.[25]

Conclusion.

Some authors consider that refractometric data provide one of the most convincing arguments against the hypothesis of complete dissociation; we see, however, that such a conclusion requires revision. In this connection it is appropriate to consider shortly to what degree the remaining ample material can be left within this hypothesis. The Debye and Hückel theory applies particularly to the field of strong electrolytes. Its conclusions, however, are of limited application. Apart from simplifications of model and of a mathematical nature, which were proved or worked out more precisely later, this theory does not take into consideration the non-Coulomb's polarising interactions. It is therefore applicable quantitatively only to dilute solutions and in solvents with small dielectric constants its field of application is in concentrations, which are accessible only with difficulty for precise measurement.

Numerous examples show nevertheless that it agrees with experiment without any corrections for incomplete dissociation, especially in the light of later more precise measurement or more precise theoretical treatment, *e.g.*, the equations of Gronwall, La Mer and Sandved.[26]

The author's work with Trachtenberg,[27] provides an example of the good applicability of the complete dissociation hypothesis and of Debye and Hückel's theory to solvents with small dielectric constants; in this the activity coefficients of lithium chloride in *iso*-amyl alcohol were found by studying the distribution of this electrolyte between alcohol and water. This example is interesting for two reasons: firstly, it is one of the very few cases described in literature of the precise measurement of strong electrolyte activity in solvents with small dielectric constants and secondly LiCl, being a typical strong electrolyte in water, reveals a number of electrochemical anomalies in non-aqueous solvents, which were often ascribed to complex formation and association.

In the region 0·0006-1·74 mol./1000 g. solvent, we have found Hückel's formula to apply well:

$$\log f = -\frac{5{\cdot}48\sqrt{c}}{1 + 4{\cdot}61\sqrt{c}} + 2{\cdot}20c \quad (25^\circ)$$

The limiting coefficient 5·48 corresponds, according to the theory, to the dielectric constant $D = 16$, which approximates to $D = 20\text{-}21$ for *iso*-amyl alcohol, saturated with water. The distribution is well within the thermodynamical dependence $a_1^{M_1}/a_2^{M_2} = const = 263$, the quantity M_1/M_2 having for different concentrations values decreasing on dilution from 1·12 to the limiting value 1·00. This indicates that LiCl completely dissociated in *iso*-amyl alcohol, just as in water.

Other methods of study of strong electrolytes solutions show no reason for departing from the complete dissociation hypothesis. The use of Wien's effect and of scattering of light gave (since the General Discussion of the Faraday Society in 1927) important results. The demonstration of the former is slightly marked by anomalies,[28] which were in part explained only recently.[29] The absence of vibration Raman-frequencies, corresponding to undissociated molecules, remains a great argument in favour of the complete dissociation of strong electrolytes in a solution.

Two exceptions (nitric acid and sulphuric acid) may readily be explained by the fact that these two substances, though non-polar in the pure state, are subjected on dilution to intramolecular regrouping, which converts them into the ionogenous form (*e.g.*, according to the scheme recently proposed by Rao).[30] Absorption of light in solutions of strong electrolytes also fails to reveal the presence of any perceptible quantities of non-dissociated molecules, except again in the case of nitric acid.[31]

In solvents with very small dielectric constant, the possibility of association must be taken into account, as follows, *e.g.*, from much of Kraus's and Fuoss's recent work. The question remains open, however, whether this association must be considered as a real process or merely as a matter of calculation as Bjerrum [32] thinks. The boundary region between strong and weak electrolytes is indistinct, and here special regard must be given to the complex dissociation of those electrolytes which belong to the potential type, according to the classification of Ulich.[33]

Summing up, we see that there are at present no sufficient grounds for rejecting the Sutherland-Bjerrum hypothesis, and that refractivities which were sometimes put forward as the most potent argument against it do not by any means give sufficient grounds for its rejection.

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[15] W. Geffcken and D. Price, *Z. physikal. Chem.*, *B*, 1934, **26**, 81.

[16] W. Geffcken, A. Kruis and Ch. Beckmann, *Z. physikal. Chem.*, *B*, 1933, **20**, 398.

[17] O. Redlich and P. Rosenfeld, *Z. physikal. Chem.*, *A*, 1931, **155**, 1; *Z. Elektroch.*, 1931, **37**, 705; W. Geffcken, *Z. physikal. Chem.*, *A*, 1931, **155**, 1.

[18] See also W. Geffcken and D. Price, *loc. cit.*[15]

[19] Redlich and Rosenfeld's review shows that it takes place for a number of electrolytes other than KCl.

[20] *E.g.*, from chemical interaction by contamination from the air or glass.

[21] A. E. Brodskii and J. M. Shershever, *loc. cit.*[5]

[22] A. E. Brodskii, K. Fajans, W. Geffcken and J. M. Shershever, *Sowphys.*, 1934, **5**, 153, 155, 157, 160, 166, 168; K. Fajans and W. Geffcken, *Z. physikal. Chem.*, *B*, 1933, **23**, 428; R. Fajans and R. Lühdemann, *Z. physikal. Chem.*, *B*, 1935, **29**, 150; and the answer to the last paper by Brodskii, etc., *Acta Physicochim. U.S.S.R.*, 1935, **3**, 692.

[23] It is known that the apparent refractivity of dissolved ions greatly differs from the actual refractivity of free ion because of the water dipoles present.

[24] A. E. Brodskii, A. M. Sack and S. F. Besuglii, *Sowphys.*, 1934, **5**, 146; *Acta Physicochim. U.S.S.R.*, 1935, **2**, 215; *J. Chem. Physics*, 1935, **3**, 449.

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[27] A. E. Brodskii and F. I. Trachtenberg, *Compt. Rend. Acad. Sc. U.S.S.R.*, 1934, **1**, 492.

[28] M. Wien and J. Schiele, *Physikal. Z.*, 1931, **32**, 545.

[29] L. Onsager, *J. Chem. Physics*, 1934, **2**, 598. The possibility of such an explanation was first shown by V. S. Finckelstein, *Trans. V-Physico-Chem. Synopsis in the U.S.S.R.*, 1929, 92.

[30] J. Ramankrishna Rao and C. S. Rao, *Nature*, 1936, **137**, 580; concentrated HNO_3 gives frequencies, characteristic of $NO_2 . HO$ (A. Dadieu and K. W. F. Kohlrausch, *Naturwiss.*, 1931, **20**, 690; H. Aderhold and H. E. Weiss, *Z. Physik.*, 1934, **88**, 83) and concentrated H_2SO_4 frequencies characteristic of $SO_3 . (H_2O)_2$ (J. Ramankrishna Rao, *Ind. J. Physics*, 1933, **8**, 123.

[31] H. v. Halban and J. Eisenbrandt, *Z. physikal. Chem.*, *A*, 1928, **132**, 402, 431; Ph. Gross and A. Goldstein, *Monatshefte Chem.*, 1930, **55**, 316; H. Fromherz and Kun-Hou-Lih, *Z. physikal. Chem.*, *A*, 1931, **153**, 321; G. Scheibe, *Z. Elektrochem.*, 1928, **34**, 497; *Z. physikal. Chem.*, *B*, 1929, **5**, 355, and others.

[32] N. Bjerrum, *Trans. Faraday Soc.*, 1927, **23**, 433; *Berichte*, 1929, **62**, 1005; see also Ph. Gross and O. Halpern, *J. Chem. Physics*, 1934, **2**, 188.

[33] H. Ulich, *Z. Elektrochem.*, 1933, **39**, 483.

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*GENERAL DISCUSSION.**

Dr. G. W. Brindley (*Leeds*) said: The comparison given by Professor Stewart in Tables II. and III. of Δv (the effective volume of ions in solution), and the sum of the spherical volumes $(v_1 + v_2)$, suggests that the volumes are much greater in solution than in the crystalline state, especially for the salts of potassium, rubidium and caesium, but if Δv is compared with the true molecular volume in the solid state, the opposite result is obtained. It is desirable when making such a comparison to calculate the molecular volume for the same type of crystal structure in every case. Since most of the halides have the NaCl-type of structure, it is convenient to compare Δv with the molecular volumes for this type of structure; corrections which are easily made must then be applied to the observed molecular volumes of CsCl, CsBr and CsI which have a different type of structure. The results are shown in the accompanying table, which gives $\Delta v / V$, where V is the true molecular volume in NaCl-type structure.

	Cl.	Br.	I.
Li	0·85	0·95	1·06
Na	·62	·71	·84
K	·71	·77	·84
Rb	·75	·78	·83
Cs	·76	·78	·80

These values may be considered as follows: In passing from CsCl to NaCl, $\Delta v / V$ gradually decreases; this is an indication that as the size of the positive ion decreases, the surrounding water molecules are more firmly attached to it. There is a similar variation in passing from CsBr to NaBr, though it is less marked because Br^- contributes more to the total volume than does Cl . In the case of the iodides, $\Delta v / V$ is practically constant. The values for the Li salts are strangely different; the abnormalities arise from the Δv values which are seen from Professor Stewart's tables to be larger for the Li salts than for the corresponding Na salts.

* On three preceding papers.

A further point of interest is that if one compares Δv with the molecular volumes in the CsCl-type of structure, a very close agreement is obtained; for CsCl, CsBr and CsI, the molecular volumes in the solid state are 69·4, 78·8 and 94·8 while the corresponding Δv values are 63·8, 74·4 and 92·5.

Professor J. A. Prins (*Wageningen*) said: Professor Stewart has made important experimental contributions to the study of liquid structure chiefly by the X-ray method. In this connection he introduced the word "cybotaxis" for the molecular arrangement in liquids. Though in my opinion little is gained by introducing a new name it is possible that it may have been useful to others. At any rate there is no real objection to it. A new name, however, does not exempt us from our duty to state exactly what the arrangement in question is like. Here in my opinion Professor Stewart has made a false step in introducing cybotactical *groups*. This term suggests (and is intended to suggest) that the imperfect order in liquid may be described as at least a momentary mixture of almost perfectly ordered small groups and completely disordered parts. Now this view ("micro-crystalline hypothesis") may be compared to the old theory of electrolytic dissociation, where a definite percentage of the molecules (changing its individuals every moment of course) is considered to be undissociated, the rest being completely dissociated. In the simplest case, however, of strong electrolytes we know this conception to be wrong, the ionic interactions being describable in a *statistical* way only. In my opinion, the molecular arrangement in simple liquids can also be described in a statistical way only ("quasi-crystalline hypothesis"). As in the theory of weak electrolytes, however, special cases may arise in which the "group"-idea applies. Exceptional cases of this kind are enumerated in my paper. Also in the case of mixtures not too far above the critical temperature of perfect miscibility, a clustering of molecules of the same kind might be expected. This may be called "sub-arrangement" and will presumably occur when solvent and solute have no strong affinity.[34] On the other hand a strong and far-reaching affinity would cause a "super-arrangement" of the solute in the solvent, as described in my paper.

Dr. J. D. Bernal (*Cambridge*) said: Professor Stewart seems to have evinced a certain misunderstanding as to the conclusions which Fowler and I reached as to the hydration of ions. In all cases we found monovalent ions associated only with four water molecules instead of the six or eight that Professor Stewart attributes to us. The confusion may have arisen from a certain theoretical discussion earlier in the paper as to the maximum number of water molecules that could sterically fit round any ion, but, of course, our main thesis was that this maximum was not reached in actual water owing to the stability of the tetrahedral co-ordination due to the hydroxyl bonds.

Dr. P. Gross (*Wien*) said: Although some contradictory reports, especially concerning the rôle of anions have been reported in the past [35] and are still reported in the paper of Albright and Williams (*viz.*, the rôle of iodine ions), Debye's point of view as a whole seems to me to be corroborated, Complete numerical agreement is not to be expected for theoretical reasons already explained elsewhere.[36] But I think one should make use of Debye's picture apart from salting out effect in connection with various questions concerning solutions of electrolytes and non-electrolytes. Such an application, which in its turn may give a more or less direct proof of Debye's view, is the investigation of the change of ion-mobility brought about by non-electrolytes.

Almost all the observations, recorded hitherto, of the relation between changes of viscosity and the mobilities of small ions were based on the use of substances which reduce the dielectric constant of the solvent water.[37] They show that the mobility of small ions is not reduced to such an extent as is to be expected from the increase in viscosity. In these cases, in the vicinity of the ion, the concentration of the added non-electrolyte, and consequently the viscosity, is lower than on the average. Bearing this in mind, we can easily explain the effect described. (The approximate constancy of the product viscosity × ionic-mobility in some cases of very large ions does not contradict our view, since at their surface, on account of their large radius, the concentration of the non-electrolyte does not appreciably deviate from its average value.)

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[34] *Cf.* H. K. Ward, *J. Chem. Physics.*, 1934, **2**, 153.

[35] H. von Halban, G. Kortüm and M. Seiler, *Z. physik. Chem.*, *A*, 1935, **173**, 462.

[36] See Ph. Gross, *Ber. Ak. Wissensch. Wien* II. b, 1929, **138**, 445; O. Halpenr and Ph. Gross, *J. Chem. Physics*, 1933, **2**, 184.

Since the dielectric constant of aqueous glycine solutions increases markedly with the concentration, the glycine molecules will accumulate in the vicinity of the ions. We must, therefore, expect the mobility of the ions to be decreased to a greater extent than is due to the increase in macroscopic viscosity. My colleague, Fraulein Wischin, experimented with KCl as electrolyte. The important factors are the conductivities at infinite dilution extrapolated from very dilute solutions. There are also theoretical and experimental reasons for taking the glycine concentration as low as possible, so that the effect becomes very small and the measurements must be carried out with the highest possible accuracy. I am not yet satisfied with the accuracy in all cases, so I refrain from giving figures. The experiments, however, show beyond doubt that the mobility decreases in all cases to a greater extent than is due to the change in viscosity. From this standpoint one easily can understand that there is a relation between the variation of the product viscosity × mobility due to the choice of the solvent and the *structure* of the solvent *liquid*.

Professor K. Fajans (*Ann Arbor*) (*communicated*) : Professor Brodskii mentions the refractometric experimental results obtained in the laboratory for Physical Chemistry at Munich since 1927, and the explanation which my collaborators and I have proposed. I want to emphasise that recently an important addition to the former results has been published by A. Kruis, partly in collaboration with W. Geffcken.[38] The dispersion of the solutions of strong electrolytes was measured for a wide range of concentrations In the theoretical discussion by Kruis of the dispersion data the same genera ideas were successfully used as were obtained from the study of the change with concentration of the molecular refractivity of electrolytes. In concentrated solutions, where this change is approximately linear the main effect has been ascribed to the formation of combinations of oppositely charged ions in direct contact with each other with no water molecules between them. In solutions below approximately 1-2 *N* where, in the case of some electrolytes a maximum of refractivity occurs, as was shown by Brodskii and also at Munich, another effect must come into play. It has been assumed that this effect is due to the interaction between the ions and the more remote molecules of the solvent water.

The communication of Professor Brodskii does not appear to give valid reasons for changing our opinion. However, two remarks may be added. First, our point of view is not as divergent from that of Bjerrum as would appear from the discussion of Brodskii. Bjerrum himself introduced, in 1926, the idea of association of ions in the solutions of strong electrolytes. Secondly, I refer to the new publications of G. Kortüm[39] whose very exact measurements of the light absorption give no indication for the association of oppositely charged ions in dilute solutions of strong electrolytes. It will be of great interest to determine whether the difference between the refractometric results at high concentrations and these of Kortüm are due to the different range of concentrations used or if more profound reasons are responsible.

[37] See C. W. Davies, *Conductivity of Solutions*, London, 1933, p. 123.

[38] *Z. physikal Chem.*, 1936, **34**, 1-95.

[39] *Ibid.*, *B*, 1935, **30**, 317 ; 1935, **31**, 137 ; 1936, **33**, 1, 243.

Dr. A. R. Martin (*London*) (*communicated*): The conclusion drawn from the experiments of Brodskii and Trachtenberg on the distribution of lithium chloride between water and *iso*-amyl alcohol that this salt is completely dissociated in the latter solvent is open to some doubt. The *iso*-amyl alcohol was inevitably saturated with water. Traces of water in non-aqueous solvents are known to have a considerable influence on the properties of dissolved electrolytes,[40] and this would be expected to be particularly marked in the case of such a hygroscopic substance as lithium chloride.

Professor G. W. Stewart (*Iowa*), in reply, said: Professor Prins opines the introduction of the word "group" has been a false step and presumably because that concept is not found in the current approximations of theoretical investigations. Present experiments in X-ray diffraction require time integration and, to be satisfactory, quantitative theories are not expected to use directly a temporary inhomogenity. There is no need for abandonment of detail in concept, although it be not of immediate service in theoretical studies, since it has proved and may continue to prove suggestive. But Professor Prins is incorrect in his statement of my intention as to the meaning of the word "group." "Cybotaxis" was introduced very definitely to avoid a crystalline concept and "group" to avoid a microcrystalline impression. I presume no one would doubt that, in a liquid, there is, at any instant, a space variation in the degree of orderliness, with the configuration at any point changing with time. The magnitude of this space variation undoubtedly differs with substances and physical conditions and cannot be known without some method of measurement. The term "group" was used to express the fact of this variation, as it does not necessarily imply any definite magnitude in the change of the degree of order from inside a region where it is an optimum to an adjoining region where it is smaller. In the early studies in liquid structure, the magnitude of this variation of the degree of order was probably over-emphasised through the picture drawn. But the intention was clearly just as stated.

My thanks are due to Dr. Bernal for his correction. The article of Bernal and Fowler is perfectly clear and there should be no misunderstanding except by a much too hasty reference without a fresh reading. In referring to the discussion of Bernal and Fowler on hydration, instead of saying, "In the view of Bernal and Fowler, etc." the words should have been, "It is in harmony with the discussion of Bernal and Fowler for one to expect that the hydration of Li^+ and Na^- may be different from that of the other alkalis, perhaps due to a difference in the permanence of the attachment. This is perhaps the explanation of the decreasing ratio $\Delta v/(v_1 + v_2)$ in Table II." This change makes no essential alteration in the discussion.

Professor A. E. Brodskii (*Dnepropetrovsk*), in reply: Professor Bjerrum's point of view on the association of strong electrolytes is clearly pointed out in his papers [41] above mentioned. It is at present difficult to bring refractometric data into direct relation with the absorption measurements in solutions of electrolytes. At any rate, the insensitivity of light absorption to the state of dissolved electrolytes does not necessarily require the same behaviour for refraction as Dr. Kortüm believes.[42]

It seems to me difficult and unfruitful to make assumptions as to the state of dissolved electrolytes from refractometric data, until the similar behaviour of the refraction curves for both electrolytes and non-electrolytes is explained. In any event, the curve of urea, which is similar to the curves of strong electrolytes, cannot be explained by complete or incomplete dissociation.

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[40] Ulich, Hartley and co-workers.

[41] See also N. Bjerrum, *Det Kgl Danske Vid. Sels.*, VII., Nr. 9, 1926.

[42] G. Kortüm, *Das optische Verhalten gelöster Electrolyte*, 1936, p. 60.

In reply to Dr. Martin : Of course the *iso*-amyl alcohol was saturated with water, and this is taken into account in our calculations. Clearly this comparatively small amount of water cannot essentially change the state of dissociation of LiCl in this alcohol. The water-saturated alcohol remains a solvent with small dielectric constant, in which the dissociation is found to be complete.

A NOTE ON THE DIAMAGNETISM OF SALTS IN AQUEOUS SOLUTION.

By G. W. Brindley, M.Sc., Ph.D., *University of Leeds*, and F. E. Hoare, Ph.D., *University College, Exeter*.

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1. Introduction.

The interest attached to measurements of the diamagnetism of salts in solution from the standpoint of the theory of solutions depends on the close connection which exists between the susceptibility of an atom or molecule and the spatial distribution of its electrons. For a spherically symmetrical atom, the susceptibility per gram atom, χ, is given by $\chi = -(Ne^2/6mc^2)\Sigma\overline{r^2}$, where $\overline{r^2}$ is the mean square distance of an electron from the nucleus and the summation extends over all the electrons.[1] This expression may also be written in the form $-(Ne^2/6mc^2)\int_0^\infty r^2 . U(r)dr$, where $U(r)$ denotes the number of electrons per unit radial distance. It is seen from these equations that χ depends mainly on the distribution of electrons at large values of r, and since these will be mainly involved in any deformation of the atom, it follows that diamagnetic measurements may be useful in indicating atomic or molecular deformations.

The determination of the susceptibilities of diamagnetic salts in solution is usually based on an equation of the type $\chi = c\chi_s + (1 - c)\chi_w$ where χ_s and χ_w are the susceptibilities of the dissolved salt and solvent respectively, and c is the concentration. In calculating χ_s, it is usual to assume that χ_w is the same as for pure water ; this cannot be tested directly but from indirect evidence it appears to be invalid owing to the effect of the dissolved ions on the water molecules. It is this question which will be considered in the present note. From a detailed review of the available experimental data, mainly for the halides of the alkali metals and the alkaline earth metals, we have selected a set of values which in general are probably accurate to within 1 per cent. and which form a reliable basis for discussing the susceptibilities of ions in aqueous solution.

2. The Determination of Ionic Susceptibilities for Solutions and the Question whether the Susceptibilities are Additive.

The question of additivity is best tested as follows[2]: If the susceptibility of one ion, say H^+ in HCl, is taken as x, then from the experimental data we can find the best average values for the susceptibilities

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[1] See, for example, E. C. Stoner, *Magnetism and Matter*, Ch. IX.

[2] The advantages of proceeding in this way have been discussed by the writers elsewhere, see ref. 4.

TABLE I.—IONIC SUSCEPTIBILITIES, PER GRAM-ION, FOR IONS IN SOLUTION, $-\chi \times 10^6$.

(*a*)	H^+	$-0{\cdot}1 + x$				
	Li^+	$3{\cdot}4 + x$				
	Na^+	$9{\cdot}3 + x$	F^-	$6{\cdot}6 - x$	Mg^{+2}	$6{\cdot}9 + 2x$
	K^+	$17{\cdot}7 + x$	Cl^-	$21{\cdot}4 - x$	Ca^{+2}	$12{\cdot}9 + 2x$
	Rb^+	$26{\cdot}7 + x$	Br^-	$32{\cdot}7 - x$	Sr^{+2}	$22{\cdot}2 + 2x$
	Cs^+	$41{\cdot}0 + x$	I^-	$50{\cdot}5 - x$	Ba^{+2}	$35{\cdot}2 + 2x$

Mean value of $x = -3{\cdot}7 \pm 0{\cdot}2$ (see text),

(*b*)	H^+	$-3{\cdot}8 \pm 0{\cdot}2$				
	Li^+	$-0{\cdot}3$ „				
	Na^+	$5{\cdot}6$ „	F^-	$10{\cdot}3 \pm 0{\cdot}2$	Mg^{+2}	$-0{\cdot}5 \pm 0{\cdot}4$
	K^+	$14{\cdot}0$ „	Cl^-	$25{\cdot}1$ „	Ca^{+2}	$5{\cdot}5$ „
	Rb^+	$23{\cdot}0$ „	Br^-	$36{\cdot}4$ „	Sr^{+2}	$14{\cdot}8$ „
	Cs^+	$37{\cdot}3$ „	I^-	$54{\cdot}2$ „	Ba^{+2}	$27{\cdot}8$ „

More approximate values.

(*c*)	Be^{+2}	$-0{\cdot}4$	$(NH_4)^+$	16	$(ClO_3)^-$	32
	Zn^{+2}	9 ?	$(OH)^-$	9	$(ClO_4)^-$	33
	Cd^{+2}	$20{\cdot}7$	$(NO_3)^-$	$20{\cdot}8$	$(SO_4)^{-2}$	43

of other ions in terms of x. The results obtained by proceeding in this way are given in Table I. (*a*); the final value for H^+ is not x but $(-0{\cdot}1 + x)$ due to the incorporation of data for HBr and HI in the averaging process. The question of additivity is then tested by comparing the sums of the appropriate ionic susceptibilities with the observed values; we find that the agreement between the observed and calculated values comes well within the limits of uncertainty of the experimental data for a large number of salts.[*] The susceptibilities of ions in solution can, therefore, be taken as additive within these limits. It remains now to determine x in order to obtain the absolute susceptibilities.

A similar problem has been discussed by Bernal and Fowler[3] in connection with their theory of ionic solutions; they required the effective volumes of dissolved ions and took the *relative* volumes of Cs^+ and Cl^- to be the same as in the crystal CsCl. They find then that there is a normal relation between ionic volumes in solution and in the solid state only for the large univalent ions, and that for all other ions the effective volumes in solution are much smaller than in the solid state or even negative, so that " the conclusion almost forces itself that in the first case the ions are not hydrated and in the second they are to a greater or less degree." They also show from considerations of the potential energy of dissolved ions in water, that no hydration is to be expected for the large univalent ions, Rb^+, Cs^+, Cl^-, Br^- and I^-. That there is a strong attachment of water molecules to small and multiply charged ions is shown both by calculations of the potential energy and by the fact that these ions have very small or even negative effective volumes in solution. The fact that the large univalent ions have volumes which are closely the same in solution as in the crystalline state, suggests that the susceptibilities may also be similar, but abnormalities may be expected in the case of the smaller and multiply charged ions since these ions are definitely hydrated.

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[*] For the sake of brevity, we are omitting all discussion of the actual experimental data.

[3] J. D. Bernal and R. H. Fowler, *J. Chem. Physics*, 1933, 1, 515.

These ideas can be tested by comparing the susceptibilities of Cs and Rb halides in solution and in the solid state, but the difference in co-ordination number must be considered. CsCl, CsBr and CsI crystals have a structure with co-ordination number 8. In solution, according to Bernal and Fowler,[3] the ions probably have 4-fold co-ordination. The susceptibilities of the crystalline salts can also be calculated for co-ordination number 6 by using the susceptibilities found for the ions in crystals of the rocksalt type.[4] For the Rb salts we have data corresponding to co-ordination numbers 4 and 6 only. The results are set out in Table II. It seems reasonable to conclude from these observations that the ions Cs$^+$, Rb$^+$, Cl$^-$, Br$^-$ and I$^-$ have susceptibilities in solution which are not very different from those found in the corresponding crystals; the slightly larger values found for the solutions fit in with the smaller co-ordination number.

TABLE II.—SUSCEPTIBILITIES OF SALTS IN SOLUTION AND IN THE CRYSTALLINE STATE, $-\chi \times 10^6$.

	Salts in Solution. C.N. 4.	Diff.	Crystals. NaCl Type. C.N. 6.	Diff.	Crystals. CsCl Type. C.N. 8.
CsCl . .	62·4	3·1	59·3	2·6	56·7
CsBr . .	73·7	4·1	69·6	2·4	67·2
CsI . .	91·5	5·8	85·7	3·1	82·6
RbCl . .	48·1	1·7	46·4	—	—
RbBr . .	59·4	3·0	56·4	—	—
RbI . .	77·2	5·0	72·2	—	—

If the *ratio* of the susceptibilities of two ions, such as Cs$^+$ and Cl$^-$, is taken to be the same in solution as in the solid state with co-ordination number 6, then we can calculate the unknown quantity x in terms of which the ionic susceptibilities have been expressed. For the crystal values we use those which we have recently obtained from a study of the alkaline halides.[4] Proceeding in this way for the six Rb and Cs salts in turn, we obtain the following mean value for x:

$$x = -3·7 \pm 0·2.$$

Using this value we obtain the ionic susceptibilities given in Table I. (*b*). Estimates of the susceptibilities of a few other ions have also been made; these are given in Table I. (*c*) and are probably much less accurate than those given in Table I. (*b*).

3. Comparison of the Susceptibilities of Ions in Solutions and in Crystals.

Ideally it would be best to compare the susceptibilities of the dissolved ions with the corresponding values for *free* ions, but the latter cannot be estimated or calculated theoretically with sufficient accuracy for the purpose. We shall therefore compare the susceptibilities of the dissolved ions with the values for crystals. For the alkaline halide ions we shall use the values obtained for crystals of the rocksalt type.[4] For the ions Mg^{+2}, Ca^{+2}, Sr^{+2} and Ba^{+2}, we shall use values recently obtained from the halides of these ions;[5] for other ions we have estimated the susceptibilities from the available experimental data. Table III. gives the susceptibilities of the dissolved ions, χ_{sol}, and of the crystalline ions, $\chi_{crystal}$, and the difference $\Delta\chi = \chi_{sol} - \chi_{crystal}$. This table also gives the ionic packing radii, R, (mainly Zachariasen's values),[6] and the probable degree of hydration of the ions in water, C (*i.e.*, the number of water molecules surrounding each dissolved ion), taken from the paper of Bernal and Fowler.[3]

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[4] G. W. Brindley and F. E. Hoare, *Proc. Roy. Soc., A.*, 1935, **152**, 342.

It is seen from Table III. that $\Delta\chi$ varies between large negative values for small and doubly charged ions and positive values for large singly charged ions. To see the significance of this variation of $\Delta\chi$, we must consider the changes involved in passing from the crystalline to the dissolved state. This may be regarded as taking place in two stages, *viz.*, crystalline state → free state → dissolved state. Then $\Delta\chi$ will depend on

(*a*) the transition from the crystalline to the free state,

(*b*) the effect of the water molecules on the ion when it is dissolved, and

(*c*) the effect which the ion has on the surrounding water molecules.

Consider first the case of small ions, such as H^+, Li^+, Be^{+2}. . . . These have small susceptibilities in both the solid and the dissolved state because of their small size; in consequence the change of susceptibility due to (*a*) and (*b*) must be very small in absolute magnitude, though perhaps large relatively. But in view of their small size and, in some cases, their double charge, these ions will have the largest effect on the surrounding water molecules. $\Delta\chi$ will therefore depend mainly on (*c*). In the extreme case of H^+, which has zero susceptibility, $\Delta\chi$ must depend entirely on (*c*).

At the opposite extreme, we have the case of I^-, which, owing to its large size and single charge, will have the least effect on surrounding water molecules; (*c*) will then be a minimum and (*a*) and (*b*) will be relatively more important. We may expect that surrounding a free ion either by other ions in a crystal or by water molecules in a solution will diminish its susceptibility, and the sign of $\Delta\chi$ will then depend on whether (*a*) or (*b*) is the greater. It seems reasonable to consider that the susceptibility will be diminished more in the case of a crystalline ion owing to the tighter binding and larger co-ordination number in the solid state, and if this is the case, then χ_{sol} will be greater then $\chi_{crystal}$ and $\Delta\chi$ will be positive, which is what we find. In this way it seems possible to give a qualitative explanation of the variation of the $\Delta\chi$ values.

The change in the susceptibility of a water molecule due to the presence of a dissolved ion will arise owing to a change of the electron distribution of the molecule brought about by the intense field surrounding the ion; in particular, any deformation of the *outermost* parts of the molecule will result in a change of susceptibility. Very approximately, the change of susceptibility may be taken as proportional to the field at the "boundary" of the ion, which is equal to n/R^2 if R is the effective radius and n is the charge in electron units. The change of susceptibility will also depend on the degree of hydration. We should therefore expect $\Delta\chi$ to be some function of C and n/R^2. In Table III. the ions have been arranged in order with the largest value of Cn/R^2 at the top and the smallest at the bottom of the table. It is seen that $\Delta\chi$ varies from negative to positive values in a fairly steady way as Cn/R^2 decreases. The large negative value of $\Delta\chi$ for Zn^{+2} is probably not significant but arises from uncertainties in the χ_{sol} and $\chi_{crystal}$ values. Be^{+2} is the only ion which quite definitely does not fit into this scheme and this again may be due to errors in the experimental data, which are very meagre for this ion.

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[5] F. E. Hoare and G. W. Brindley, a paper on the susceptibilities of the halides of Mg, Ca, Sr and Ba, to be published soon.

[6] W. H. Zachariasen, *Z. Krist.*, 1931, 80, 137.

Table III. also includes data for a few polyatomic ions, but the χ_{sol} and $\chi_{crystal}$ values are too uncertain for these ions for the differences to be reliable; but it is perhaps significant that for all these ions $\Delta\chi$ is positive, which points to these ions not being hydrated in solution.

TABLE III.

Ion.	*R.*	*n.*	*C.*	Cn/R^2.	$\chi_{sol.}$	$\chi_{crystal.}$	$\Delta\chi$.
H^+	—	1	—	—	−3·8	0	−3·8
Be^{+2}	0·39	2	4	52·6	−0·4	0·3	−0·7
Mg^{+2}	0·71	2	6	23·8	−0·5	4·3	−4·8
Zn^{+2}	0·83	2	6	17·4	9 ?	16 ?	−7 ?
Ca^{+2}	0·98	2	6	12·5	5·5	10·7	−5·2
Cd^{+2}	1·03	2	6	11·3	20·7	24 ?	−3·3 ?
Sr^{+2}	1·15	2	6	9·12	14·8	18·0	−3·2
Li^+	0·68	1	4	8·64	−0·3	0·7	−1·0
Ba^{+2}	1·31	2	6	6·96	27·8	29·0	−1·2
Na^+	0·98	1	4	4·16	5·6	6·1	−0·5
K^+	1·33	1	4	2·26	14·0	14·6	−0·6
F^-	1·33	1	4	2·26	10·3	9·4	0·9
Rb^+	1·48	1	4	1·83	23·0	22·0	1·0
Cs^+	1·67	1	4	1·43	37·3	35·1	2·2
Cl^-	1·81	1	4	1·22	25·1	24·2	0·9
Br^-	1·96	1	4	1·04	36·4	34·5	1·9
I^-	2·19	1	4	0·83	54·2	50·6	3·6
$(NH_4)^+$	—	—	—	—	16	13·5	2·5
$(NO_3)^-$	—	—	—	—	20·8	19·6	1·2
$(ClO_3)^-$	—	—	—	—	32	26	6
$(ClO_4)^-$	—	—	—	—	33	30	3
$(SO_4)^{-2}$	—	—	—	—	43	38	5

4. Conclusions.

The main points of this note are :—

(i) The susceptibilities of ions in solution are closely additive.

(ii) The susceptibilities of large univalent ions in solution are comparable with their values in the crystalline state (see Table II.).

(iii) The susceptibilitiss of small and bivalent ions in solution are much smaller than in the crystalline state and sometimes are effectively negative owing to the action of the ions on the water molecules.

(iv) It is shown that $\Delta\chi = \chi_{sol} - \chi_{crystal}$ varies progressively with Cn/R^2 where n/R^2 is the field at the boundary of the ion and C is the degree of hydration.

Finally it should be mentioned that for the sake of brevity we have omitted all discussion of the experimental data and no comparison has been made between the ionic susceptibilities given in Table I. and the observed results ; a more detailed discussion will be given elsewhere.

GENERAL DISCUSSION.

Dr. A. R. Martin (*London*) said: It is difficult to measure the diamagnetism of a dissolved substance accurately, except at high concentrations. Were the concentrations at which Dr. Brindley and Dr. Hoare worked so great that ion-pairs might be formed?

Dr. G. W. Brindley (*Leeds*), in reply said: The majority of susceptibility measurements are made for solutions of moderate strength. The results are not likely to be influenced appreciably by direct interaction between positive and negative ions in solution for the following reasons:—

(i) The fact that the susceptibilities of dissolved ions are additive implies that the susceptibility of each kind of ion is independent of what other ions there may be in solution.

(ii) Susceptibility-concentration curves are found to be linear in practically every case where careful measurements have been made for a wide range of concentration; if anion-cation interaction occurred appreciably at the higher concentrations, a departure from a straight line would be expected.

(iii) The experimental measurements are generally made for such concentrations that the ratio of the number of water molecules to dissolved ions is large enough for each dissolved ion to be surrounded by a fully co-ordinated group of water molecules. In all cases, therefore, and particularly for ions which are permanently hydrated, there appears to be little chance of direct anion-cation interaction.

Professor J. A. Prins (*Wageningen*) asked: What is the susceptibility of pure water and how is it related to the $\Delta\chi$ values in Table III.?

Dr. G. W. Brindley (*Leeds*) in reply, said: The susceptibility of pure water, per gr. mol., is usually taken as 12·96 which is based on the value 0·72 for the susceptibility per gram; these figures are to be multiplied by -10^{-6}. In comparing this value for water with the $\Delta\chi$ values in the last column of Table III., it must be remembered that the $\Delta\chi$ values apply to the co-ordinated group of water molecules surrounding the ion; it will be more useful therefore to compare the value for water, 12·96, with $\Delta\chi/C$.

SUMMARY OF THE DISCUSSION.

By J. A. V. Butler.

Part I. Pure Liquids.

The discussion on pure liquids opened with a comprehensive account by London of the forces between atoms and molecules and particularly of the dispersion force which bears his name. The earlier theories of molecular interaction, *viz.* Keesom's orientational force between molecules having permanent dipoles and Debye's induction effect, failed to provide an explanation of the general van der Waals' attractive forces, which must be of an additive nature. London gives a very lucid account of the origin of the dispersion effect, which is ascribed to the rapid variations of charge distribution round apparently symmetrical atoms, giving rise to "an orchestra of dipoles" which act by induction on the electronic systems of other atoms.

The question of structure was opened by Bernal's important paper which gives in outline a geometrical theory of the liquid state. The initial problem is the expression of the average distribution of molecules round a given molecule, which is formulated in terms of (*a*) a co-ordination number, *i.e.*, the number of immediate neighbours of a given molecule, (*b*) an irregularity function, which Bernal regards as the fundamental characteristic of the liquid state. When this distribution has been formulated the total energy of the liquid can be expressed in terms of the same variables and the entropy is also determined by the irregularity function, so that the free energy is also determinable. The stable state of the liquid at a given temperature is that having the minimum free energy, and it is easily seen that in general the equilibrium configuration may vary with the temperature, giving rise to a configurational factor in the specific heat, compressibility, etc. Perhaps the most interesting feature of this theory is the light it throws on the process of melting. If a liquid differs from a solid merely in its greater degree of thermal agitation and disorder, it is difficult to see why the process of melting is so sharp. In this theory the irregularity factor of liquids causes the free energy of the liquid to increase more rapidly with the temperature than that of the corresponding solid and thus a temperature is reached at which equilibrium between two essentially distinct phases is possible.

The process of melting was considered from other points of view. Simon discussed the possibility of a critical point between solids and liquids and cited evidence showing the increasing similarity of solid and liquid phases at increasing temperatures and pressures. It was admitted however that the evidence is inconclusive and since at very high pressures breakdown of the electronic shells of atoms may take place, the question may have no practical reality. Frenkel also discussed the question from the point of view of the amplitude of vibrations in solids and diffusion in liquids.

The heat capacity of liquids was discussed by Bartholomé and Eucken, who gave a modification of the Planck-Einstein calculation for solids, with a special form of the potential function. It was interesting to find that even in the case of hydrogen and helium, they found it necessary to assume a slight " association," varying with the temperature, which Bernal pointed out is equivalent to his configurational change. Brillouin suggested that the transverse vibrations of the solid are replaced by rotations in the liquid, giving a limiting heat capacity for a liquid of $2R$. The excess would have to be accounted for in other ways, among which a kind of configurational change, *viz.* the break up of ultra-microscopic solid clusters was suggested.

In the next part of the discussion emphasis was laid on the great similarity of different simple liquids. Bauer, Magat and Surdin showed that a single function of a reduced temperature, involving the critical and freezing-points, was capable of representing various properties of a large number of simple liquids. Hudleston showed that a simple formula of the compressibility applies with considerable exactness to a number of liquids. Trouton's rule in its various forms and Langmuir's very general vapour pressure formula [1] also provide evidence in the same direction. Newton and Eyring went even further in suggesting a vapour pressure relation, based on a partition function for liquids, in which the factors for rotations and vibrations are the same as in the gas, and the main characteristic of the liquid (apart from the energy of condensation) is its free volume. This leads to the conclusion that at constant volume the heat capacities of the liquid and gas are the same. The fact that such simple assumptions lead to a fair measure of success shows the great uniformity of many different liquids.

As might be expected, viscosity (like the melting-point with reference to solids) is more sensitive to differences of structure, and Ward showed that the viscosity relations lend themselves to a classification of liquids. Changes in the slope of the $\log \eta - 1/T$ curve are regarded as indicating a change in the type of co-ordination, and it is suggested that B in $\eta = Ae^{-B/T}$ will be proportional to the latent heat of fusion when no fundamental change of co-ordination occurs on melting, but not otherwise.

It was unfortunate that no general survey of the results hitherto obtained from the application of X-rays to liquid structure was available, but both Prins and Randall gave recent examples of the structure analysis

[1] *J. Amer. Chem. Soc.*, 1932, 54, 2798.

and discussed the general interpretation of the scattering curves. They insist that the only information to be obtained is the distribution function for molecular distance round a given molecule, and this is to be deduced from the shape of the scattering curve when appropriate corrections have been made.

Finally some new experimental methods of investigating liquid structures were discussed. Magat showed that in the Raman spectra of liquids new frequencies appear which must be ascribed to intermolecular vibrations. Errera discussed absorption by dipolar substances in the far infra-red, at frequencies $> 1/\tau$ ($\tau =$ relaxation time), which is complementary to previous work on the absorption and dispersion of Hertzian waves ($\nu < 1/\tau$). Very pronounced bands were found in this region and the absorption was much greater than that calculated from results in the Hertzian region by the Debye dispersion formula. The absorption of ultrasonic waves in liquids has been studied by Claeys, Errera and Sack and by Lucas and Biquard. While no appreciable dispersion of sound has been detected, owing apparently to the relaxation time of liquids being considerably smaller than in gases, considerable absorption occurs, which cannot be accounted for on the classical theory. The most probable explanation seems to be a frequency variation of the compressibility.

Part II. Solutions.

In the introductory paper Hildebrand surveyed the effect of the intermolecular forces in solutions of two non-polar substances and discussed, in the light of the evidence now available, the validity of his well-known relation which gives the deviation from Raoult's law in terms of the difference between the square roots of the energies of vaporisation per c.c. of the two substances. It appears that although qualitative agreement is obtained, the observed deviations are often appreciably greater than the calculated. This may be due either to a partial failure of the assumptions, *e.g.* that which takes the potential of two unlike molecules as the geometrical mean of the potentials of the individual molecules or, as the subsequent discussion showed, to the assumption that the entropy of solution is the same as for ideal solutions.

Guggenheim pointed out that the number of cases in which Raoult's law has been shown to hold over the whole range of concentration is small, but it was suggested that the evidence is not quite so meagre as might appear since indirect proofs are available in other cases. He also discussed the conditions necessary for the validity of Raoult's law. It is known that the two substances must mix without heat or volume change. A consideration of the effect of molecular size when these conditions are fulfilled led to the conclusion that unless the difference of size is considerable, the effect will hardly be detectable.

Scatchard discussed the relations between the heat, volume change and entropy of solution. The volume change is usually proportional to the deviation from Raoult's law,[3] and Scatchard expresses it as the product of the compressibility and the excess of free energy over that of the corresponding ideal solution, which is borne out at least roughly by the limited amount of exact data available. When two substances mix without change of volume the entropy of mixing is taken as that of an ideal solution, but when a volume change occurs this gives rise to an additional entropy change, which is evaluated as the volume change multiplied by the ratio of the coefficients of thermal expansion and compressibility. The entropy of solution was also discussed by Evans, who showed, from a consideration of solubility curves, that the entropy of solution is proportional to the heat of solution; further evidence on the same point for volatile substances was given by the writer.

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[3] *Cf.* Hildebrand, "Solubility," 1936, p. 59.

It thus appears probable that whenever there is a heat effect on the formation of a solution, the entropy will differ from that of the ideal solution. If this proves to be general, Hildebrand's suggested subdivision of " regular solutions," (in which there are deviations from Raoult's law arising from the heat of mixing, but the entropy of the solution is that of an ideal solution) does not exist. The point will no doubt receive further consideration.

The next part of the discussion dealt mainly with solutions of polar molecules in non-polar and polar media. Martin showed that his expression for the variation of the free energy of a polar molecule with the dielectric constant of the medium holds even when the changes of dielectric constant are produced by the polar molecules themselves, and Banks gave data drawn from distribution coefficients showing a similar variation in different solvents. Wolf discussed the heats of dilution of alcohols, etc., in non-polar solvents, and Butler and Harrower gave a comparison of the behaviour of the aliphatic alcohols and halides in non-polar solvents. Although having similar dipole moments the activity coefficients of the two types differ greatly, suggesting a different type of interaction in the two cases.

Complex formation between two polar molecules, *e.g.* chloroform and ether, as shown by dielectric constant measurements, was considered by Glasstone, and a considerable amount of discussion followed on the nature of association in liquids and the bending forces of complex molecules. Bernal suggested a useful distinction between associated liquids (in which all the molecules are bound together by forces other than the van der Waals' forces, *e.g.* water, in which there is a network of hydroxyl bonds throughout the liquid) and those in which small groups of two or more molecules only are united in a complex molecule. A somewhat similar distinction between molecular " solutions " and " mixtures " was made in Wolf's paper. At present there are few criteria for distinguishing these cases. Thus, although it is known that in dilute solutions in non-polar solvents carboxy-acids exist mainly as double molecules, it is not clear whether in the undiluted acids or alcohols there is a more extensive structure, such as that suggested by Sidgwick.[8] Information can be obtained from the changes on dilution of various properties of which the following are mentioned in various parts of the discussion : X-ray diffraction curves, which show a long spacing in pure alcohols and acids which is not obtained with the corresponding halides (Stewart) ; infra-red and Raman spectra, which show bands which disappear on dilution (Errera and Magat) ; heats of dilution and the accompanying volume changes (Wolf).

In the discussion on the nature of the binding forces in such complex molecules as $CHCl_3 . (CH_3)_2O$, the point at issue was whether the dipolar forces are sufficient when account is taken of the shapes of the molecules, or whether a hydrogen bond such as $CCl_3—H—O(CH_3)_2$ exists. The result seems inconclusive and it would appear that a more exact knowledge of the electronic distributions in the two molecules than is given by their dipole moments and rough sizes is required before the question can be solved.

The discussion finished with some papers on the more specialised field of strong electrolytes.

The survey is necessarily incomplete, and omits many points of importance, and the writer trusts that any misrepresentations which may have arisen in an attempt to sum up in a few words the salient points of the discussion will be forgiven. The discussion as a whole covers most of the directions in which progress is being made, and will be found to provide many sign-posts for future work.

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[8] Annual Reports, *Chem. Soc.*, 1934, p. 42.

*GENERAL DISCUSSION.**

Professor J. Frenkel † (*Leningrad*) (*communicated*) : In reply to Dr. W. R. van Wijk : The equation $\overline{\delta^2} = 6Dt$ can be applied to the *elementary* displacements, *i.e.*, the smallest displacements whose directions are not correlated with those of the preceding or succeeding ones. In the case of a gas for example the elementary displacement corresponds to the mean free path $\bar{\delta} = l$. Using Clausius law one finds

$$\overline{\delta^2} = \int_0^\infty \delta^2 e^{-\delta/l} \frac{d\delta}{l} = 2l^2,$$

whence

$$D = \frac{\overline{\delta^2}}{6t} = \frac{1}{3}\frac{l^2}{t} = \frac{1}{3}lv.$$

where v is the mean velocity—in accordance with the well-known result of the kinetic theory of gases.

The application of the equation $\overline{\delta^2} = 6Dt$ to the elementary zig-zags seems thus to be justified in the case of diffusion in a liquid.

In reply to Mr. Bernal : If it is true—as I claim it, and as Mr. Bernal seems to concede—that at negative pressures the degree of disorder *in a crystal* must increase, then the gap between a crystal and a liquid must decrease with increasing negative pressure, or more exactly with increasing expansion. The way such an expansion can be realised in practice is a question that must be considered from the point of view of the experimental check of the theory, and not from that of its internal consistency (I have devised a method based on the propagation of ultrasonic waves of high amplitude, which eliminates the possibility of cracks and can reveal transitions from the solid state to the liquid one and *vice versa* during the succeeding phases of the oscillations). Mr. Bernal's final argument that at low temperatures the continuous transformation from crystal to liquid is excluded because thermodynamic equilibrium is impossible, refers again to the practical side of the question and not to the theoretical one. One might argue, for the same reason, that the intermediate states assumed by van der Waals' theory between the liquid and gaseous ones, corresponding at low temperatures to high negative pressures, are physically unrealisable.

In reply to Professor Simon : My assertion that there must be a critical point terminating the melting curve at low temperatures is based on the undisputable fact that the thermal pressure of a solid must decrease as the temperature is lowered. This point is considered in detail in my paper on the theory of fusion and crystallisation.[4] It follows also from the numerical calculations of Hertzfeld and Göppert Mayer [5] for the case of solid argon. Their results are represented graphically by the curves of Fig. 2 on p. 999 of their paper, which shows a minimum of the total pressure as a function of the volume at higher temperatures (100° C. for example) and no such minimum for lower ones. While the above authors interpreted this minimum as corresponding to the melting-point, I claim that it must be accompanied by a maximum of the pressure, the wave-line portion of the p-v isotherm representing unstable states which are replaced in reality by the discontinuous transition, represented by $p = const.$ Thus the experimental data used by Hertzfeld and Göppert Mayer in their calculations for argon seem to support my view. The case of helium is yet too uncertain to be used for or against the theory. The extrapolation to absolute zero, showing two different phases with different volumes and energies does not seem conclusive inasmuch as unstable intermediate states have been excluded from the outset.

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* Contributions received too late for inclusion in proper order.

† See p. 78. For reply of Mr. Bernal to 5th paragraph see p. 45.

[4] *Acta Physicochimica U.R.S.S.*, 1935, 3, 913.

[5] *Physic. Rev.*, 1934, 46, 991.

There is one point in Mr. Bernal's theory which it is difficult to accept. According to this theory the co-ordination number, that is the number of nearest neighbours around each atom must be a whole number, which can assume the values 14, 12, 10, etc. Now, on the other hand, this number is not assumed to remain constant as the temperature is raised, but to vary in *a continuous* way—so long as there are no discontinuities in the curve of the specific heat of a liquid or its volume as a function of the temperature. Now it is clear that the co-ordination number in Bernal's theory cannot vary in a continuous way. This inherent contradiction seems a very grave difficulty for Bernal's theory. Under such conditions it seems safer to cling to the Kratki-Prins theory at least for temperatures not far away from that of melting.

Again with regard to the evaluation of the specific heat of liquids. Near the melting-point it approximates to that of the corresponding solid (somewhat exceeding it though). This fact cannot be explained in a simple way on the basis of Prins' or Bernal's theory, so long as they do not introduce the notion of provisional equilibrium positions about which the molecules vibrate. This could be done in the simplest way by treating the arrangement described by the above theories as the *average arrangement of the equilibrium positions*, and by introducing in addition the thermal vibrations about these positions. I hope to consider this point in a future communication.

Professor H. Hellmann (*Moscow*) (*communicated*) : * It seems that a misunderstanding has set in in my discussion with Professor London. I would like therefore to make a few remarks in connection with the reply of Professor London.

To the points (1) and (2) of the reply of Professor London I can establish that, in the derivation of my formula (3), I do not have to make the assumption that the total eigenfunction of an atom or molecule is a product of the eigenfunctions of the individual *electrons*, but only that it can be written as the product of the eigenfunctions of the individual *shells*. The many electron problems of each shell can be assumed to be rigorously solved. The interaction of the various shells with one another under this assumption permits only an approximation of the type of Hartree. In the perturbation calculations of Quantum Chemistry one seldom has to do with such modest simplifying assumptions. From this assumption, together with the symmetry of the shells, it follows at once, that the polarisibility of a rare gas is additively composed of the polarisibilities of its shells. By the way, Massey and Buckingham[6] found that my formula agrees well with the existing data concerning the interaction between alkali metal vapours and the rare gases.

In complicated molecules the polarisibilities may be localised with the same justification as the valences. This approximation of localisation is used in chemistry with good results, one therefore will scarcely give it up because it cannot be 100 per cent. rigorously proved. I think that the remaining arbitrariness is smaller than the always present uncertainty which arises from the extrapolation of the asymptotical law to the small distances.

In point (3) Professor London says that the Slater-Kirkwood law gives a too small attraction for rare-gas-like ions and therefore the change of the lattice type at CsCl cannot be explained. I have not succeeded in confirming this on the basis of my formula (3), which for rare-gas-like ions slightly differs from the Slater-Kirkwood formula. One obtains the original estimation of Born and Mayer from (1), if one places for I_1 and I_2 the ionisation energy and the electron affinity. Thus, for the interaction between Cs^+ and Cl^- it follows:

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* See p. 44.

[6] *Nature*, 1936, 138, 77.

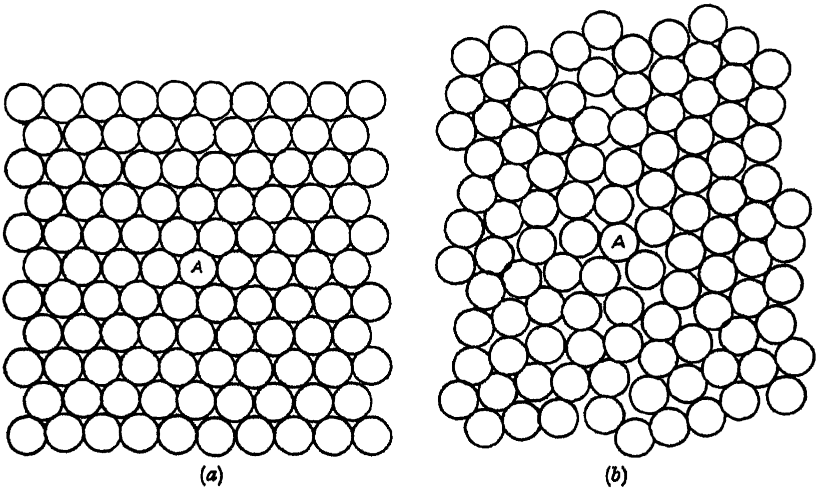
$$\frac{1}{1/T_1 + 1/T_2} = \frac{540 \times 87}{540 + 87} = 74{\cdot}9 \text{ k. cal.} \qquad . \quad . \quad (7)$$

Using the I values after (2) and $\alpha(Cs^+) = 2{\cdot}35$ Å^3, $\alpha(Cl^-) = 3{\cdot}05$ Å^3 $N = 8$ one obtains:

$$\frac{1}{1/T_1 + 1/T_2} = \frac{389 \times 443}{389 + 443} = 207 \text{ k. cal.} \qquad . \quad . \quad (8)$$

According to Born and Mayer a doubling of the dispersion forces in comparison with (7) suffice to explain the change of lattice type at CsCl. A comparison of (8) with (7) shows that we have indeed attained a 2·76 times greater attraction. The average interaction between equally charged pairs is obtained from (1) and (2) with only a factor of 1·35, in comparison with the original estimation of Born and Mayer. Since the interaction between the variously charged ions is decisive, it cannot be doubted that we arrive at the right lattice type for CsCl from equations (1) and (2). This simple formula yields thus the same result as the complicated evaluation of the whole dispersion curve of the crystal (Mayer) according to the London formula in its most rigorous form. Perhaps Professor London can explain the difference between our numerical results. I have not been able to find the cause for this.

Professor J. A. Prins (*Wageningen*), in reply,* said: I am glad to note that Professor Stewart in applying the word "group" to the molecular arrangement in liquids only means to indicate that the degree of order shows fluctuations in space and time. In this way the difference with the statistical description would reduce to a mere question of language. It should be observed that the existence of fluctuations ("groups") *is* taken into account in the statistical theory. Indeed, its influence on small angle scattering was a principal point in the first paper of Zernike and the author and in the (otherwise imperfect) theory of Raman and Ramanathan.



(*a*) (*b*)

FIG. 5.†—(*a*) and (*b*) contain the same number of circles. In (*a*) every circle is surrounded by 6 others; in (*b*) the circle A is surrounded by 5 but, apart from this, the utmost effort has been made to achieve regularity, but without success.

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* See page 267.

† See page 37 (Bernal).

Contents.

PAGE

Part I. Structure and Molecular Forces in Pure Liquids . . 1

Pure Liquids and Liquid Mixtures. (General Introductory Paper.) By James Kendall 2

General Discussion.—Dr. S. Glasstone, Professor K. L. Wolf, Professor J. Kendall 8

The General Theory of Molecular Forces. By F. London . . 8

An Attempt at a Molecular Theory of Liquid Structure. By J. D. Bernal 27

General Discussion.—Professor H. Hellmann, Professor K. L. Wolf, Dr. M. Magat, Mr. J. D. Bernal, Professor F. Simon, Professor E. Bauer, Professor J. A. Prins, Professor J. H. Hildebrand, Professor F. London 40

The Dependence on Temperature of the Specific Heat (C_v) of Monatomic Liquids. By E. Bartholomé and A. Eucken . . 45

On Thermal Agitation in Liquids. By Leon Brillouin 54

General Discussion.—Dr. E. Bartholomé, Dr. M. Magat, Mr. J. D. Bernal, Professor M. Born, Professor L. Brillouin, Dr. F. London 55

On the Liquid State and the Theory of Fusion By J. Frenkel . 58

On the Range of Stability of the Fluid State. By F. Simon . . 65

A Partition Function for Liquids. By Roy F. Newton and Henry Eyring 73

General Discussion.—Professor J. A. Prins, Dr. M. Magat, Dr. W. R. van Wijk, Dr. J. A. V. Butler, Professor J. H. Hildebrand, Mr. J. D. Bernal, Professor F. Simon, Professor H. Eyring 78

Reduced Temperature and General Properties of Pure Liquids. By E. Bauer, M. Magat and M. Surdin 81

General Discussion.—Professor J. H. Hildebrand, Mr. J. D. Bernal, Professor E. Bauer, Dr. R. J. W. Le Fèvre, Professor F. Simon, Mr. F. C. Frank, Mr. Magat 86

The Viscosity of Pure Liquids. By A. G. Ward 88

Intermolecular Forces of Normal Liquids. By L. J. Hudleston . 97

General Discussion.—Professor J. Kendall, Dr. R. J. W. Le Fèvre, Dr. L. Brillouin, Mr. J. D. Bernal, Mr. A. G. Ward, Mr. L. J. Hudleston 103

The Determination of Structure in Liquids by X-Ray Methods. By J. T. Randall 105

The Identity of Structure in Liquid Lead and Bismuth. By J. T. Randall and H. P. Rooksby 109

Some New Results and General Interpretation of Diffraction by Amorphous Substances. By Professor J. A. Prins . . . 110

PAGE

General Discussion.—Dr. E. Bauer, Dr. M. Magat, Professor J. A. Prins, Professor F. G. Donnan, Mr. E. A. Guggenheim, Professor J. H. Hildebrand, Dr. R. J. W. Le Fèvre, Dr. J. D. Bernal, M. M. Mathieu 112

Raman Spectra and the Constitution of Liquids. By Michel Magat 114

Structure of Liquids Studied in the Infra-Red. By J. Errera . . 120

The Diffusion and Absorption of Ultrasonics in Liquids. By René Lucas and Pierre Biquard 130

Absorption of Ultrasonic Waves in Liquids. By J. Claeys, J. Errera and H. Sack 136

General Discussion.—Dr. H. Sack, Professor J. Errera, Dr. E. Bartholomé, Mr. C. R. Bailey, Mr. J. D. Bernal, Dr. M. Magat, 141

Part II. Structure and Molecular Forces in Solutions . . 144

Intermolecular Forces in Solutions (Introductory Paper). By Joel H. Hildebrand 144

The Theoretical Basis of Raoult's Law. By E. A. Guggenheim . 151

General Discussion.—Professor J. Kendall, Dr. M. Magat, Dr. R. J. W. Le Fèvre, Professor W. E. Garner, Dr. P. Gross, Professor J. H. Hildebrand, Dr. A. Klinkenberg, Dr. S. Glasstone, Professor G. Scatchard, Mr. E. A. Guggenheim . 156

Change of Volume on Mixing and the Equations for Non-Electrolyte Mixtures. By George Scatchard 160

The Laws of Solubility. By M. G. Evans 166

General Discussion.—Professor J. H. Hildebrand, Dr. J. A. V. Butler, Professor M. Polanyi, Mr. M. G. Evans . . . 168

The Activities of Some Aliphatic Alcohols and Halides in Non-Polar Solvents. By J. A. V. Butler and P. Harrower . . 171

On Association, Heat of Mixing and Miscibility Gaps. By K. L. Wolf 179

General Discussion.—Professor K. L. Wolf, Professor G. Scatchard, Dr. J. A. V. Butler 190

Dipole Interaction in Mixtures of Benzene with some of its Polar Derivatives. By A. R. Martin. 191

General Discussion.—Dr. A. R. Martin, Dr. J. A. V. Butler, Dr. R. J. B. Marsden 198

"The Structure of Some Molecular Complexes in the Liquid Phase." By Samnel Glasstone 200

General Discussion.—Professor J. Errera, Dr. M. Magat, Dr. R. J. W. Le Fèvre, Dr. A. R. Martin, Mr. J. D. Bernal, Dr. E. B. Ludlam, Professor Henri, Dr. C. F. Goodeve, Professor H. Hellmann, Professor J. H. Hildebrand, Professor J. Kendall, Dr. S. Glasstone 206

Dipole Solvation. By W. H. Banks 215

Complex Formation. By Geo. Glockler 224

PAGE

The Energy and Entropy of Hydration of Organic Compounds. By J. A. V. Butler 229

General Discussion.—Mr. C. R. Bury, Dr. G. Salomon, Dr. J. D. Bernal, Professor F. G. Donnan, Professor J. A. Prins, Dr. J. A. V. Butler 237

Effect of Ionic Forces shown by the Liquid Structure of Alkali Halides and their Aqueous Solutions. By G. W. Stewart . 238

Electrical Forces between Ions and Neutral Molecules in Aqueous Solution. A Study of the "Salting-Out" Effect. By Penrose S. Albright and J. W. Williams 247

The Refractometric Curves and the State of Dissolved Strong Electrolytes. By A. E. Brodskii 256

General Discussion.—Dr. G. W. Brindley, Professor J. A. Prins, Dr. J. D. Bernal, Dr. P. Gross, Professor K. Fajans, Dr. A. R. Martin, Professor G. W. Stewart, Professor A. E. Brodskii . 264

A Note on the Diamagnetism of Salts in Aqueous Solution. By G. W. Brindley and F. E. Hoare 268

General Discussion.—Dr. A. R. Martin, Dr. G. W. Brindley, Professor J. A. Prins 273

AUTHOR INDEX.*

Albright, G. S., **247**.
Bailey, C. R., 142.
Banks, W. H., **215**.
Bartholomé, E., **45**, 55, 57, 141.
Bauer, E., 43, **81**, 87, 112.
Bernal, J. D., **27**, 42, 45, 56, 79, 80, 86, 103, 113, 142, 208, 210, 237, 265, 279.
Biguard, P., **130**
Born, M., 56.
Brillouin, L., **54**, 57, 103.
Brindley, G. W., 264, **268**, 273.
Brodskii, A. E., **256**, 267.
Bury, C. R., 237.
Butler, J. A. V., 78, 168, **171**, 190, 199, **229**, 238, **273**.
Claeys, J., **136**.
Donnan, F. G., 113, 238.
Errera, J., **120**, **136**, 141, 143, 206, 208.
Eucken, A., **45**.
Evans, M. G., **166**, 170.
Eyring, H., **73**, 80.
Fajans, K., 266.
Fèvre, R. G. W. Le, 87, 103, 113, 156, 207, 210, 212.
Frank, F. C., 87.
Frenkel, J., **58**, 276.
Garner, W. E., 157.
Glasstone, S., 8, 158, **200**, 213.
Glockler, G., **224**.
Goodeve, C. F., 208.
Gross, P., 157, 158, 265.
Guggenheim, E. A., 113, **151**, 159.
Harrower, P., **171**.
Hellmann, H., 40, 208, 278.
Henri, V., 208.
Hildebrand, J. H., 44, 79, 86, 113, **144**, 157, 168, 170, 209, 212.
Hoare, F. E., **268**.
Hudleston, L. J., **97**, 104.
Kendall, J., **2**, 103, 156, 212.
Klinkenberg, A., 158.
London, F., **8**, 44, 57.
Lucas, R., **130**.
Ludlam, E. B., 208.
Magat, M., 42, 56, 78, **81**, 87, 113, **114**, 143, 156, 206.
Marsden, R. J. B , 199.
Martin, A. R., **191**, 198, 199, 208, 267, 273.
Mathieu, M., 114.
Newton, R. F., **73**.
Polanyi, M., 170.
Prins, J. A., 43, 78, **110**, 113, 114, 238, 265, 273, 279.
Randall, J. T., 8, **105**, **109**.
Rooksby, H. P., **109**.
Sack, H., **136**, 141.
Salomon, G., 237.
Scatchard, G., 159, **160**, 190.
Simon, F., 42, **65**, 80, 87.
Stewart, G. W., **238**, 267.
Surdin, M., **81**.
Ward, A. G., **88**, 104.
Wijk, W. R. van, 78.
Williams, J. W., **247**.
Wolf, K. L., 8, 42, **179**, 190.

* The references in heavy type indicate papers submitted for discussion.

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THE RECOMBINATION-VELOCITY OF FREE ATOMS.

By E. Rabinowitch.

Received 7th September, 1936.

Efficiency of Triple Collisions in Recombination of Hydrogen and of the Halogens.

In previous papers [1] we determined the velocity of recombination of the atoms of iodine and bromine in the gas-phase, with the molecules He, A, N_2, O_2, CH_4, CO_2 and C_6H_6 acting as " third bodies " X in the reaction :

$$A + A + X \rightarrow A_2 + X \quad (A - \text{Br or I}) \qquad . \quad . \quad (1)$$

The calculated velocity- constants C_1 of the equation

$$-\frac{d[A]}{dt} = C_1[A]^2[X] \qquad . \quad . \quad . \quad . \quad (2)$$

are given in Table I., together with the velocity-constant of the reaction $H + H + H_2 \rightarrow 2H_2$, determined by Steiner and Wicke and by Amdur and Robinson.[2]

TABLE I —Velocity-constants ($C_1 \times 10^{32}$) of the Reaction $A + A + X \rightarrow A_2 + X$.

(Concentrations in molecules per c.c.)

X = A =	He.	A.	H_2.	N_2.	O_2.	CH_4.	CO_2.	C_6H_6
H . .	—	—	5·9*	—	—	—	—	—
Br . .	0·76	1·3	2·2	2·5	3·2	3·6	5·4	—
I . .	1·8	3·8	4·0	6·6	10·5	12	18	100

* The constants given by Steiner and Wicke ($\sim 9 \times 10^{15}$), and Amdur and Robinson ($\sim 16 \times 10^{15}$) are those of the equation $+\frac{d[A_2]}{dt} = \textit{Const.}\,[A]^2[X]$, with concentrations in *mols*. per c.c. They must be multiplied by $2/(6 \times 10^{23})^2$ for comparison with our values. A source of uncertainty in the hydrogen-constants is the rôle played by the *atoms* as third bodies, the concentration of H-atoms in active hydrogen being a relatively high one.

The constants given in Table I. are on the whole unexpectedly high. The usual estimate is " one collision in 1000 is a triple one under atmospheric pressure." Table II. shows, however, that, for instance, in the case of the reaction $I + I + CO_2 \rightarrow I_2 + CO_2$, one collision I + I in sixty is a "recombining" one; the results obtained with C_6H_6-vapour,

---

[1] E. Rabinowitch, H. L. Lehmann, *Trans. Faraday Soc.*, 1935, **31**, 689 ; E. Rabinowitch, W. C. Wood, *Trans. Faraday Soc.*, 1936, **32**, 907 ; *J. Chem. Physics*, 1936, **4**, 497.

[2] W. Steiner, F. W. Wicke, *Z. physikal. Chemie, Bodenstein-Band*, 1931, 817 ; W. Steiner, *Z. physikal. Chemie, B*, 1932, **15**, 249 ; T. Amdur, A. L. Robinson, *J. Amer. Chem. Soc.*, 1933, **55**, 1395, 2615.

TABLE II.—PROPORTIONS OF RECOMBINING COLLISIONS ($\gamma \times 10^3$) TO THE TOTAL NUMBER Z OF DOUBLE COLLISIONS A + A UNDER ATMOSPHERIC PRESSURE OF THE GAS X.

H : $\sigma_H = 2{\cdot}5 \times 10^{-8}$ cm. $Z_{H+H} = 3{\cdot}5 \times 10^{-10}[H]^2$.
Br : $\sigma_{Br} = 4{\cdot}5 \times 10^{-8}$ cm. $Z_{Br+Br} = 1{\cdot}25 \times 10^{-10}[Br^2]$
I : $\sigma_I = 5{\cdot}2 \times 10^{-8}$ cm. $Z_{I+I} = 1{\cdot}3 \times 10^{-10}[I]^2$.

A = \ X =	He.	A.	H_2.	N_2.	O_2.	CH_4.	CO_2.	C_6H_6.
H . .	—	—	2·3	—	—	—	—	—
Br . .	0·82	1·4	2·2	2·7	3·4	3·7	5·7	–
I . .	1·7	3·6	3·9	6·3	10	12	17	97

extrapolated to atmospheric pressure, would even require every tenth collision I + I to be a triple one.

The Statistical Factor.

Fig. 1 shows the interaction-energy of two iodine atoms.[3] The lowest curve, $^1\Sigma$, corresponds to the ground state of the molecule. The other curves known from spectroscopical data are $^1\Pi$ and $^3\Pi_{2,\,1,\,0^-}$; they possess relatively shallow minima. The total statistical weight of these five states is 8. The statistical weight of the ground-state of the iodine *atom*, $^2P_{1\frac{1}{2}}$, is 4; that of two atoms together $16 (= 4^2)$. This must be the statistical weight of all the molecular state formed adiabatically from two $^2P_{1\frac{1}{2}}$-atoms. Besides the above-mentioned states of I_2, there must, therefore, exist some additional ones, also with a total statistical weight 8, dissociating into two normal atoms. They are probably of a purely repulsive character, as shown by the upper curve in Fig. 1.

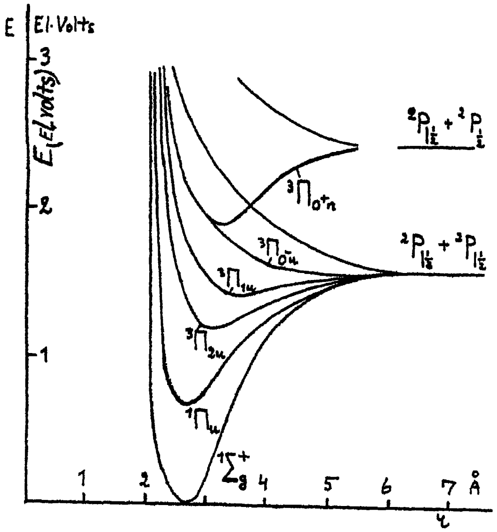

FIG. 1.

Steiner[2] supposed, that only collisions along the lowest curve, $^1\Sigma$, can lead to recombination. *A priori* probability of the state $^1\Sigma$ is 1; Steiner's assumption would thus lead to a statistical factor 1/16 in the expression for the number of possible recombining collisions.[4] The existence of other attraction curves $^1\Pi$ and $^3\Pi_2$ (not considered by Steiner) increases this factor to 5/16, because the three states $^1\Sigma$, $^1\Pi$ and $^3\Pi_2$ offer the same chance of " stabilisation " by a collision with a third body.[5] Moreover, it is by no means sure that collisions along a curve of the " flat " type $^3\Pi_1$, or even along one of the repulsion-curves, may not result in recombination. The high experimental rates observed with H-, Br- and I-atoms suggest that the passage of a third body can cause recombination even if the atoms are relatively far apart (corresponding to the outer part of the diagram in Fig. 1). In this region, the energetical differences between the single curves are very small, and the disturbing influence of the third body may easily lead to their confusion, and ultimately to a transition from a repulsion-curve to an attraction-curve. The best way of estimating theoretically the possible number of recombining collisions is to drop Steiner's statistical restriction altogether and to consider each encounter of two atoms A + A as having a certain chance to lead to a recombination by the intervention of a " third body."

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[3] This figure is taken from a paper by H. Cordes, *Z. Physik*, 1935, 97, 603.

[4] Steiner puts the statistical factor equal to 1/30, instead of 1/16. His error is to assume a $(2\Omega + 1)$-fold degeneracy for each molecular state with a moment Ω in the direction of the nuclear axis; whereas in truth part of the degeneracy

Mechanism of Triple Collisions.

In the calculation of the number of recombining collisions, we must consider the two possibilities :—

(*a*) $(A' + A'') + X$.
(*b*) $(A' + X) + A''$.

In case (*a*) the first double collision is that of two atoms A, in case (*b*) that of an A with an X.[6] One way of treating processes of this kind—used for instance by Steiner—is to consider the pair $(A' + A'')$ (or $(A' + X)$) as an unstable molecule (" quasimolecule ") (AA or AX) with a certain life-period τ_{AA} (or τ_{AX}), and to investigate the probability of a collision AA + X (or AX + A) occurring during the life-time of the " quasi-molecules." This method involves the assumption of a definite diameter of the quasi-molecules. For that of AA Steiner substituted the gas-kinetical diameter of the corresponding stable molecule A_2. This assumption ignores the fact that diameters of free atoms are strongly reduced by the formation of molecules (an H-*atom* has, according to the viscosity-measurements by Harteck, nearly the size of the whole H_2 *molecule*). Assuming, as we have done above, that recombination takes place even at comparatively large distances between the three particles, we think it better to avoid the notion of " quasi-molecules " altogether, and to consider all three partners of the triple collision as independent particles. In this case, the numbers of the triple collisions of the kinds (*a*) and (*b*) are :

$$Z_{(AA)X} = z_{AA}\tau_{AA}Z_{AX} \quad . \quad . \quad . \quad . \quad (3)$$

$$Z_{(AX)A} = z_{AX}\tau_{AX}Z_{AA} \quad . \quad . \quad . \quad . \quad (4)$$

---

is removed already by the Stark-effect of the interacting atoms. For the vector Ω, independently of its absolute value, only *two* orientations are possible ($+ \Omega$ and $- \Omega$).

[5] The rule of conservation of multiplicity will not preclude recombination by the way of the $^3\Pi$-state, if the minimum of this curve is deep enough to prevent the molecule from being dissociated by collisions before falling down into the ground state. The multiplicity-selection-rule is not a very strict one in the case of atoms as heavy as I (or even Br), and the natural life-time of the $^3\Pi$ state will not be longer than 10^{-7} sec.

[6] Kimball, *J. Amer. Chem. Soc.*, 1932, **54**, 2396, first pointed out the necessity of taking into account collisions of the kind (*b*) in discussing the recombination of hydrogen-atoms.

Z_{AA} and Z_{AX} are *total* numbers of double collisions A + A, and A + X occurring per second in a certain volume, whereas z_{AA} and z_{AX} are numbers of collisions occurring during the same time to a *single* particle A. The products $z_{AA}\tau_{AA}$ (and $z_{AX}\tau_{AX}$) are the probabilities of finding a particle A in state of collision with another A (or with an X) in any given moment.

Error is introduced into (3) and (4) by the fact that the velocities of A and X during the collisions are not identical with their mean thermal velocities, used in the calculations of Z; they may be greater or smaller, according to the shape of the interaction-curves.

Formulæ (3) and (4) show that the differences in the numbers of triple collisions in different gases X can be due, in the case of the process (*a*), to different *numbers of double collisions* A + X only. In the process (*b*), differences of this kind may be caused also by different *collision-periods* τ_{AX}. The *possible variations* of Z_{AX} are relatively small, because greater molecular diameters are usually compensated by smaller molecular velocities (due to the heavier masses). Z_{BrBr} is for instance (see Table II.) practically equal to Z_{II}, and only three times smaller than Z_{HH}. The great differences between the C_1-values for different gases X, actually observed, according to Table I., indicate that process (*b*) plays an important rôle in the recombination—at least, when less volatile gases (CO_2, C_6H_6, etc.) are involved as third bodies.

Estimation of the Collision-period.

Molecular diameters and masses are the essential quantities determining the number of *double* collisions. In the case of *triple* collisions, the most important rôle is played by the collision-periods τ. (The approximate number of double collisions can be determined by using rigid molecular models; no triple collisions at all will, however, occur to absolutely rigid molecules.) The quantities τ are characteristic of the *deviation* of the molecules from rigidity, of their " softness." A high probability of triple collisions depends not so much on a large collision-diameter as on a long " collision-path "—*i.e.*, on a great difference between the distance at which the interaction begins and the distance of nearest approach of the particles.

We shall first try to estimate roughly how long the intervals τ must be in order to explain the experimental values of C_1. We assume in this calculation gas-kinetic values for the molecular diameters σ of the particles A and X. For the atoms Br and I we take the values 4·5 and 5·2 Å., which are slightly greater than the diameters of the adjoining rare gases Kr($\sigma = 4{\cdot}28$) and Xe ($\sigma = 4{\cdot}9$ Å.). (The diameters of the uncompleted seven-electron shells of the halogen-atoms must be slightly greater than those of the eight-electron shells of the rare gases—as shown for instance by slightly smaller ionisation-potentials.) This involves the assumption that the long-range forces, which determine the beginning of a collision A + A are van der Waals' forces (whose intensity must be about the same for the pair Br + Br as well as for Kr + Kr) and *not* the exchange-forces, due to the non-saturated character of the halogen atoms. (This assumption is in agreement with the calculations by Eisenschitz and London of the long-range interaction-forces between two hydrogen atoms.)

We use the " uncorrected " values of σ, obtained from viscosity-data at room temperature. These values correspond to distances at which the interaction energy becomes of the order of magnitude of kT The differences between these values and those corrected by means of Sutherland's formula are a measure of the "softness" of the molecules, and will be used as such further below. Introducing into (3) and (4) the usual kinetic expressions for Z_{AA} and Z_{AX} and using the relations

$$Z_{AA} = \tfrac{1}{2}z_{AA}[A] \quad . \quad . \quad . \quad . \quad (5)$$

and

$$Z_{AX} = z_{AX}[A] \quad . \quad . \quad . \quad . \quad . \quad (6)$$

we obtain

$$\begin{aligned} Z_{tri} &= Z_{(AA)X} + Z_{(AX)A} \\ &= 4\sqrt{2}\pi\sigma_{AX}{}^2\sigma_A{}^2\frac{RT}{\sqrt{\mu_{AX}\cdot M_A}}[A]^2[X](2\tau_{AA} + \tau_{AX}) \quad . \quad . \quad (7) \end{aligned}$$

with the abbreviations

$$\sigma_{AX} = \frac{\sigma_A + \sigma_X}{2} \quad \text{and} \quad \mu_{AX} = \frac{M_A M_X}{M_A + M_X} \quad . \quad . \quad (8)$$

The factor 2 before τ_{AA} in (7) is due to the fact that two particles A are involved in each collision A + A. If one triple collision in $1/\beta$ results in a recombination of two atoms, the recombination-constant C_1 becomes:

$$C_1 = 8\sqrt{2}\Pi\sigma_{AX}{}^2\sigma_A{}^2\frac{RT}{\sqrt{\mu_{AX}M_A}}(2\tau_{AA} + \tau_{AX})\beta \quad . \quad . \quad (9)$$

or with $R = 8{\cdot}3 \times 10^7$ and $T = 300°$

$$C_1 = 8{\cdot}9 \times 10^{11} \times \frac{\sigma_{AX}{}^2\sigma_A{}^2}{\sqrt{\mu_{AX}M_A}}(2\tau_{AA} + \tau_{AX})\beta \quad . \quad . \quad (10)$$

Table III. contains the values of $(2\tau_{AA} + \tau_{AX})\beta$ calculated from the empirical values of C_1. They range from $0{\cdot}6 \times 10^{-13}$ (He + Br) to $2{\cdot}0 \times 10^{-12}$ sec. (CO_2 + I); the still higher value for C_6H_6 + I (about 8×10^{-12}) is very uncertain.

TABLE III.—$(2\tau_{AA} + \tau_{AX})\beta$ IN SECS. $\times 10^{13}$.

	He.	H_2.	A.	N_2.	O_2.	CH_4.	CO_2.	C_6H_6.
H . .	—	1·5	—	—	—	—	—	—
B_2 . .	0·64	1·2	2·0	3·2	4·5	3·4	6·9	—
I . .	1·2	1·7	5·0	7·3	12·5	9·6	20·0	84

We will now compare the τ-values given in Table III. with the durations of gas-kinetic collisions estimated as follows: We consider the differences $\Delta\sigma$ between the molecular diameters calculated without Sutherland's correction, and those calculated with this correction ($\Delta\sigma$ is, of course, a function of temperature). This is roughly the path which two molecules cover from the moment their interaction energy becomes commeasurable with kT ("boundary" of the interaction-field) until their directions are reversed, and back to the boundary. We assume that for two different molecules 1 and 2 this path is $\frac{(\Delta\sigma_1 + \Delta\sigma_2)}{2}$, and the velocity with which it is covered—the mean thermal velocity.

Table IV. contains the values of $\Delta\sigma$ for the different gases and the values of $2\tau_{AA} + \tau_{AX}$ calculated from them. The last column shows the values of $(2\tau_{AA} + \tau_{AX}) \times \beta$ (from Table III.). Although the whole calculation is an extremely rough one, some conclusions may be drawn from the comparison of the last two columns.

(1) In the case of $X = N_2$, O_2, CH_4 or CO_2 practically every contact between the molecular fields of the three particles $A + A + X$ results in recombination of the atoms.

(2) In the case of $X =$ He or H_2 and (to a lesser degree) in that of $X = A$ the efficiency is smaller, but the proportion of successful collisions is never much less than 1/10.

TABLE IV.—COLLISION-PERIODS, CALCULATED FROM SUTHERLAND'S CONSTANTS.

	$\Delta\sigma \times 10^8$.	$\tau_{AX} \times 10^{13}$.	$2\tau_{AA} + \tau_{AX}$ (from Sutherland's correction).	$(2\tau_{AA} + \tau_{AX})\beta$ (from Table III).
Br/Br (= Kr/Kr)	0·99	3·6	—	—
Br/He	0·63	0·5	7·7	0·6
Br/H_2	0·66	0·4	7·6	1·2
Br/A	0·85	2·2	9·4	2·0
Br/N_2	0·78	1·7	8·9	3·2
Br/O_2	0·81	1·8	9·0	4·5
Br/CH_4	0·96	1·5	8·7	3·4
Br/CO_2	1·12	3·0	10·2	6·9
I/I (= X/X)	1·50	6·5	—	—
I/He	0·88	0·7	13·7	1·2
I/H_2	0·92	0·5	13·5	1·7
I/A	1·11	2·9	15·9	5·0
I/N_2	1·04	2·2	15·2	7·3
I/O_2	1·06	2·4	15·4	12·5
I/CH_4	1·22	1·9	14·9	9·6
I/CO_2	1·37	3·6	16·6	20
I/C_6H_6	2·40	8·0	21·0	84

(3) In the case of $X = C_6H_6$, the recombination is much more rapid than could be expected from the corresponding value of $\Delta\sigma$. This can be considered as an indication that the recombination process in a $I_2 + C_6H_6$—mixture is not the simple three-body reaction

$$I + I + C_6H_6 \rightarrow I_2 + C_6H_6,$$

but some more complicated process, possibly involving complexes[7] $I . C_6H_6$.

Comparison with Experiments on Transfer of Vibrational Energy.

The recombination $A' + A''$ involves the loss by the molecule $A'A''$ of at least one vibrational quantum, transformed—completely or partially—into the relative *kinetic* energy of $A'A''$ and X. This process occurs, according to the above-discussed results, by each (or nearly each) gas-kinetic collision of A′, A″ and X. On the other hand, experiments on sound-dispersion and activation-velocity in gases (reviewed by Patat [8]) show that the excitation of the first vibrational quanta by collisions occurs only in one case out of 10^3 or 10^4 collisions in which the necessary energy is present. The same probability-factor must also apply to the inverse process—the *loss* of the first vibrational quantum by collision.

---

[7] We showed[1] that the experimental results obtained with iodine atoms and benzene molecules at first indicated strong deviations from the laws of the three-body-reaction. These deviations can be explained—see E. Rabinowitch, *Z. physik. Chemie*, *B*, **33**, 275, 1936 by convection-currents. The corrections involved in this case are, however, so large that the possibility of other effects—for instance, such due to the complexes C_6H_6I—is not altogether excluded.

A higher probability was found in experiments [9] by Franck and Wood (discussed by Franck and Eucken) and by Rössler on the influence of collisions on the resonance-fluorescence. They found nearly each gas-kinetic collision to be effective in excitation or loss of vibrational quanta of excited I_2-molecules.[10]

The explanation given by Franck was that strongly vibrating molecules have much "opener" electronic structures than the stable ones. The outer part of the potential curve of the molecule A′A″ is therefore much stronger affected by the encounter with X than the inner one. The relative nuclear movements of the atoms in an already vibrating A′A″ are therefore strongly influenced by the approach of X. After the end of the collision the molecule may easily find itself in a new vibrational state.

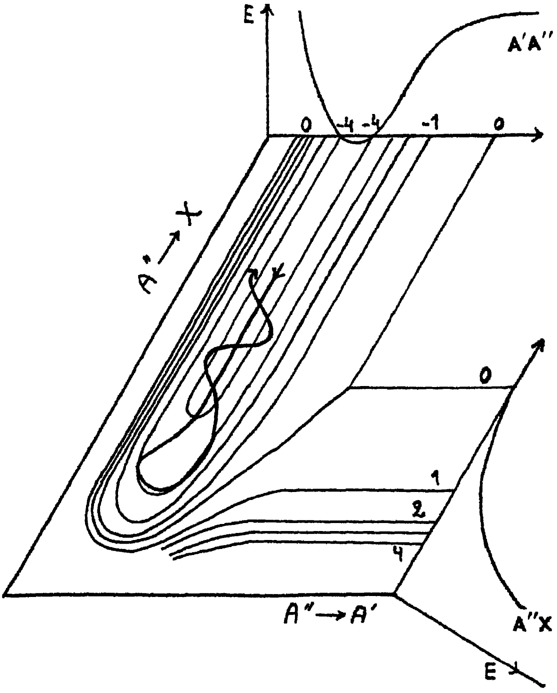

FIG. 2*a*

The results of the recombination-experiments obviously range in the same category with those of the fluorescence experiments.

Simple cases of the process in question can be discussed by means of potential surface models introduced by Polanyi and Eyring. Fig. 2 shows the surfaces for three particles of the same mass (the angle between the co-ordinates being equal to 60°), moving along a straight line. The forces between A′ and A″ are given by the curve A′A″, those between A″ and X by the curve A″X. In 2*a*, the potential energy during the triple collision is assumed to be simply the sum of the two curves. In Fig. 2*b*, the forces are the same as in Fig. 2*a*, but the contraction of the electronic system of A″ by its interaction with A′ is assumed to make the interaction range of A″ and X shorter. The cross-sections of the potential surface parallel to the axis A′A″ are therefore changed by the approach of X (this being a more detailed description of what Frank calls " a change in the potential curve of A_2 by the presence of X "). Another case of an influence of this kind is shown by Fig. 2*c*, where slight *attraction*-forces are assumed to exist between a *free* A″ and X, disappearing when A″ becomes stably bound by A′.

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[8] F. Patat, *Z. Elektrochemie*, 1936, **42**, 265.

[9] J. Franck and A. Eucken, *Z. physik. Chem.*, *B*, 1933, **20**, 460 ; F. Rössler, *Z. Physik*, 1935, **96**, 251.

[10] The conclusion by Rössler that the efficiency is sometimes *greater* than the number of gas-kinetic collisions is based on the assumpton of a life-period $\tau = 10^{-8}$ secs. for excited I_2, and on the use of molecular diameters σ corrected by means of Sutherland's formula. By assuming $\tau = 10^{-7}$ secs., and using *uncorrected* σ-values—as suggested above—all efficiencies will surely become < 1.

The process of *excitation* of a vibrational quantum of a stable molecule is described by the curve in Fig. 2*a*, that of an already strongly vibrating molecule by the curve in Fig. 2*b*, and the dissociation of a molecule already fully charged with vibration by the curve in Fig. 2*c*. The same curves, followed in the opposite direction, describe the *loss* of vibrational quanta by collisions, the last one corresponding to the case of *recombination*. (The mechanism of recombination being the one described above as

$$(A'' + X) + A'.$$

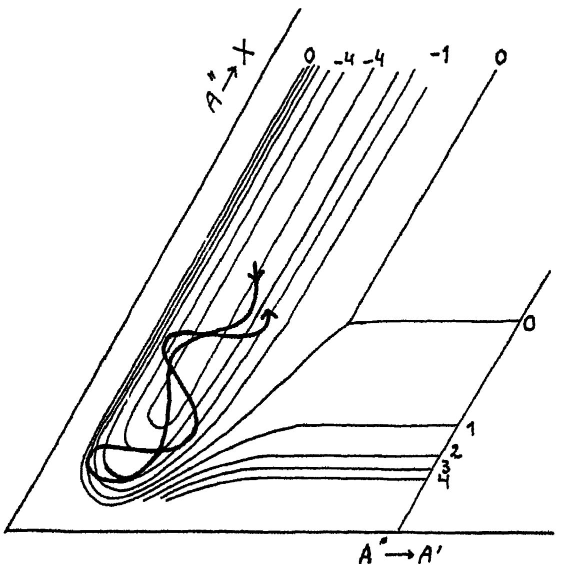

FIG. 2*b*.

It is apparent from Fig. 2, that the change in the vibrational state is connected with an *asymmetrical* deviation of the equipotential lines on both sides of the A′A″—valley. This asymmetry depends (*a*) in Fig. 2*a* solely upon the angle between the co-ordinates, *i.e.*, on the relative masses of A and X. (In the limiting case $(M_A/M_X) = \infty$ the co-ordinates will be rectangular and the asymmetry must disappear.) (*b*) In Fig. 2*b* also upon the contraction of the atoms A during the formation of A_2; (*c*) Finally, in Fig. 2*c*, in addition to the other effects also upon the existence of attraction-forces between A″ and X.

Because A is never *infinitely* greater than X, the probability of the change of the vibrational state by collision is a finite one, even in the absence of (*b*) and (*c*). The influence of (*b*) decreases the probability of the transformation of stable molecules, although probably by not more than a factor 2 or 3. There exists, however, another factor making the excitation of the first vibrational quanta more difficult, namely, their *greater size*. The vibrational quanta of stable Cl_2 and CO_2 (gases used in sound-dispersion experiments) are equal to 600-700 cm.$^{-1}$ (and thus greater than kT at room-temperature); the vibrational quanta of I_2* in Rössler's work were about 100 cm.$^{-1}$; and the quanta removed during recombination smaller still. To transfer a greater quantum, a greater asymmetry in the equipotential curves is required. Furthermore, because of the steeper ascent of the energy-curve at the nearer approach of the nuclei, as compared with the wide "fore-court" in which the energy is of the order of kT, the *path* of the system on which the necessary impulse in the direction of the axis A′A″ must be acquired is in the case of the larger quanta, a much shorter one. In other words: generally, only a part of the total collision-period can be used for the transformation of translation-energy into vibrational energy, namely, the time during which the greater part of the collision-energy is present as potential energy. This is nearly the total duration of "ordinary" collisions, but only a small part of the duration of "high-speed" collisions, which are necessary for the excitation of the lower vibrational quanta.

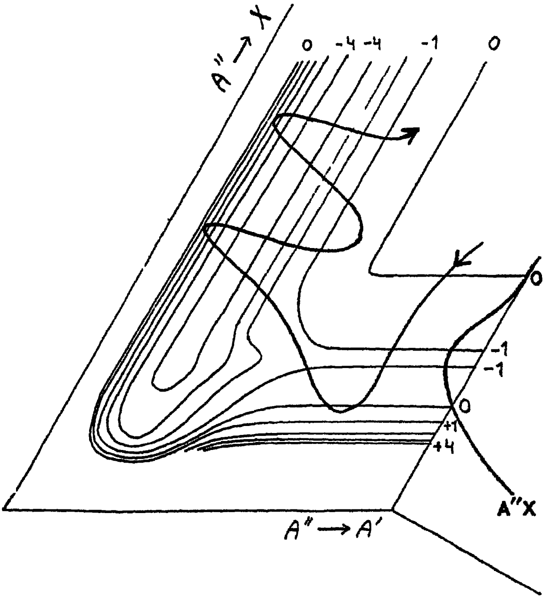

FIG. 2c.

These factors may explain differences in the efficiency of the excitation of lower and upper vibrational quanta, prior to the existence of any disturbances in the potential-curves, of the kind shown in Fig. 2c. The hypothesis of Franck, however, gives the major importance to effects of this latter kind.

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* Steiner[2] explained the high efficiency of recombination (in the case of diatomic molecules as third bodies) by quantum-mechanical "resonance"-effects. To obtain a resonance he compared the vibrational quanta which must be lost by the newly-formed molecule with an appropriate combination of vibrational and rotational quanta of the "third body." This formal use of the notion of quantum-mechanical resonance has, however, no physical meaning. Quantum-mechanical resonance-effects occur only when two different quantum states of a system, having the same energy, can be transformed one into another repeatedly during the time-interval allowed for interaction. This is only possible if the movements which cause the transformation are *swift* compared with those determining the interaction-time. In our case, the interaction-time is that of a molecular collision. Only electronic movements are swift enough to be able to cause repeated transformations during intervals of this length; therefore, only states differing by electronic quantum numbers can show resonance effects. *Vibrational* periods are, on the whole, only *slightly smaller* than the collision-durations, and rotational periods usually much *longer* than these. The notion of a "rotational quantum" has no meaning at all when applied to processes of this duration, the uncertainty with which the energy is defined being larger than the quantum itself.

That (*a*) is not *alone* essential, is shown by the deviation of the order of the efficiency of different collision-partners from the order of their masses. In the case of recombination-effects (Table I. and II.) the order of efficiency is at least generally that of the masses, although with accidental deviations (for instance, $\gamma(CH_4) = \gamma(O_2)$. In sound-dispersion and activation experiments, much greater variations in the order of efficiency has been found, indicating a greater rôle played by the individual forces between the colliding particles—*i.e.*, by effects of the kind shown in Fig. 2*c*.

It is also probable that the relative rôle of the factors (*a*), (*b*) and (*c*) depends on the angle under which the collision occurs and on its degree of excentricity.

The Recombination-Velocity of Nitrogen.

Professor Franck drew my attention to the results obtained by Lord Rayleigh [12] in experiments with active nitrogen. According to him, the nitrogen-afterglow can be observed—with walls properly "poisoned"—for hours after the interruption af the discharge. This seems to indicate that the velocity of recombination is much smaller in the case of nitrogen-atoms than in that of H, Br and I atoms. The following estimate show, however, that the difference is not a great one. The pressure of N_2-molecules was in Lord Rayleigh's experiments of the order of 10^{-2} mm., that of N-atoms probably of the order of 10^{-3} mm. The three-body-reaction-mechanism:

$$N + N + N_2 \rightarrow N_2 + N_2 \qquad . \quad . \quad . \quad (5)$$

gives

$$\frac{d[N]}{dt} = C_1[N]^2[N_2] \qquad . \quad . \quad . \quad . \quad (6)$$

For the time of "half-decay," we obtain:

$$t_{\frac{1}{2}} = \frac{1}{C_1[N_2][N]_0} \qquad . \quad . \quad . \quad . \quad (7)$$

where $[N]_0$ means the initial concentration of N-atoms. With

$t_{\frac{1}{2}} = 3600$ sec., $[N_2] = 3 \times 10^{14}$ and $[N]_0 = 3 \times 10^{13}$, we obtain

$$C_1 = 3 \times 10^{-32}$$

—which is nearly identical with the constant for the recombination of bromine-atoms with N_2 as third body, according to Table I.

Summary.

(1) The results of the determination of the velocity of homogeneous recombination of H-, Br- and I-atoms are compared, and attention drawn to the high efficiency of the triple collision-mechanism.

(2) It is suggested that no "statistical factor" shall be applied to restrict the possible number of successful triple collisions.

(3) It is shown that the collision-mechanism $(A' + X) + A''$ probably plays an important rôle besides the mechanism $(A' + A'') + X$.

(4) It is shown that the number of triple collisions depends on the sum $2\tau_{AA} + \tau_{AX}$, where τ_{AA} is the period of the collision AA and τ_{AX} that of the collision A + X. These sums can be estimated by comparing the

"uncorrected" molecular diameters with those corrected by means of Sutherland's formula. The comparison of data calculated in this way with those determined from the recombination-velocity shows the following :—

(*a*) In the case of N_2, O_2, CH_4 and CO_2 as third bodies, every gas-kinetic contact between the three particles leads to recombination.

(*b*) In the case of A the efficiency is somewhat smaller, in those of H_2 and He about ten times smaller than with the heavier gases.

(*c*) In the case of C_6H_6 the efficiency is much higher than expected.

(5) The results of recombination-experiments are compared with those obtained in experiments on sound dispersion and on resonance fluorescence. Together with the last-named, the recombination experiments show the easy conversion of vibrational energy into translational energy by collisions when *strongly vibrating* molecules are involved. This behaviour is discussed on hand of potential-surface diagrams.

(6) It is shown that experiments of Lord Rayleigh on the long life of active nitrogen do not require the assumption that the recombination of N-atoms is a much slower process than that of H, Br and I atoms.

I wish to thank most heartily Professor J. Franck for valuable discussions. I also thank Professor F. G. Donnan, F.R.S., for the possibility of working in this laboratory.

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London.

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[12] Lord Rayleigh, *Proc. Roy. Soc.*, *A*, 1935, **151**, 567.

THE SELECTIVE SORPTION OF ORGANIC LIQUIDS BY SOLID FILMS OF RAW LINSEED OIL AND STAND OIL.

By A. P. Laurie, M.A. Cantab.; D.S.C., LL.D. Edin.

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Wishing to determine the Refractive Index (R.I.) of the solid oil film in pictures of different dates, I adopted the immersion method, as the only one possible for the minute fragments of film available. The film being immersed in a liquid, and the iris diaphragm of the microscope nearly closed so as to pass convergent rays through the film, a bright line of light appears round the edge of the film. If the R.I. of the film is above that of the liquid in which it is immersed, the line of light moves inward, on raising the objective, but outward if below it. On testing the method on solid linseed oil films of a R.I. known from direct refractometer readings, and adopting the usual practice of mixing two liquids of different R.I. to obtain intermediate values, I got most irregular results. These results are most simply explained by assuming selective sorption of one of the liquids by the oil film.

If, for example, a solid film of linseed oil (μ, 1·500) is immersed in a mixture of liquid paraffin and bromonaphthalene (μ 1·520) the film gives a reading at first below but later, if left immersed, above that of the mixture. On now adding more bromonaphthalene to the mixture, the film again gives an initial reading below, and, although taking longer to reverse, a final reading above that of the mixture. On continuing to increase the amount of bromonaphthalene, a stable R.I. is at last reached well above 1·500, but also well below that of bromonaphthalene, the point of saturation of the film with bromonaphthalene having been reached, and an equilibrium established between the oil film, the liquid paraffin and the bromonaphthalene. On washing the film with petroleum ether, it returns to its original R.I.

Before investigating this sorption it was necessary to devise a reliable method for measuring the R.I of a film by the immersion method. To do this it is necessary to use a series of simple liquids of definite chemical composition having R.I. rising by small increments, so that the film is immersed in a simple liquid and not in a mixture. Thus, suppose two pure individual liquids, A and B, of definite chemical composition of μ 1·525 and 1·530 respectively; if on immersion in A the R.I. of the film is above that of A, and on immersion in B, it is below that of B, then the R.I. of the film is approximately 1·527. Even if the film sorbs A its R.I. cannot fall below that of A, and, if B is sorbed, it cannot rise above that of B, so that the possible error does not exceed ± 0·0025. For closer determination a series of simple unmixed liquids with smaller increments of R.I. must be used.

In order to investigate the phenomena produced by immersing solid oil films in mixed liquids of differing R.I., I selected as diluents liquids unlikely to be sorbed by a linseed oil film, *viz.*, liquid paraffin B.P., rectified white spirit, and raw linseed oil.

Liquid paraffin (μ 1·480) was mixed with bromonaphthalene (μ 1·657). In each case films some six months old and approximately 0·05 mm. in thickness were used, their R.I. measured in simple liquids being shown in Table I.

TABLE I.

	R.I. of Film.	Equilibrium R.I.
Raw linseed oil (Windsor and Newton's artist's oil)	1·502	1·555
Drying oil made by boiling with litharge . .	1·499	1·543
Lechertier Barbe stand oil, containing 70 per cent. of polymerised oil	1·501	1·571

The films were immersed successively in a series of mixtures of liquid paraffin and bromonaphthalene of increasing R.I., till the saturation point of the films for bromonaphthalene was reached. The equilibrium values of μ are shown also in Table I.

The remarkable difference between films of raw linseed oil and stand oil seemed worthy of special investigation, and I obtained from Messrs. Pearson, who have been most helpful to me in these experiments, a pure stand oil from which all unpolarised oil had been removed.

A film of approximately 0·05 mm. thickness and of μ 1·502 after drying for six months, gave an equilibrium R.I. of 1·580 in liquid paraffin and bromonaphthalene. The pure stand oil films were used in all subsequent experiments.

The increasing time lag in the reversal of R.I. when a film is immersed in mixtures of increasing bromonaphthalene content was plotted against the R.I., a film of pure stand oil being used. At higher R.I. values different samples of the film gave varying times, and the figures plotted are from a mean of several readings.

What is the probable nature of the phenomena observed? Three different bodies are in contact, liquid paraffin, bromonaphthalene and the film, and three bimolecular attractions or repulsions must exist; the final R.I. reading of the film, when it no longer rises above that of the mixture, must be due to an equilibrium between the mutual reactions of these three bimolecular systems.

However, there is a distinction between the behaviours of the two liquids, one of which behaves as a diluent, the other being the active liquid. The " active liquid " we define as follows : If an oil film has μ x, and if two liquids, the one of μ as much below x as the other is above x, are mixed in equal proportions by volume, so that the R.I. of the mixture is also x ; then if, on immersing the film in the mixture, its R.I. rises above that of the mixture, the active liquid is that having the higher R.I., but if its R.I. falls below that of the mixture, then the active liquid is that having the lower R.I.

TABLE II.

Linseed Oil Film in	Equilibrium R.I.	$\frac{\mu - \mu_2}{\mu_1 - \mu_2}$.
Paraffin + Bromonaphthalene .	1·555	35
Paraffin + Bromobenzene . .	1·526	42
Paraffin + Chlorobenzene . .	1·516	60
White spirit + Bromonaphthalene	1·537	25
White spirit + Bromobenzene .	1·525	40
White spirit + Chlorobenzene .	1·516	60
Linseed oil + Bromonaphthalene	1·529	18
Linseed oil + Bromobenzene .	1·525	40
Linseed oil + Chlorobenzene .	1·515	60
Pure Stand Oil Film in		
Paraffin + Bromonaphthalene .	1·580	49
Paraffin + Bromobenzene . .	1·535	57
Paraffin + Chlorobenzene . .	1·518	72
White spirit + Bromonaphthalene	1·550	31
White spirit + Bromobenzene .	1·536	49
White spirit + Chlorobenzene .	1·517	70
Linseed oil + Bromonaphthalene	1·540	25
Linseed oil + Bromobenzene .	1·531	50
Linseed oil + Chlorobenzene .	1·518	72

The Becke line observed at the surface of the film is due partly to refraction on the edge of the film, portions of which act as minute lenses, and partly to total reflection at the film-liquid interface. In one case I have found actual diffusion of the active liquid into the film, but the equilibrium R.I. seems generally to be a surface phenomenon ; the film surface is probably of an irregular spongy nature, with minute capillaries, on which there is a thin layer having optical continuity and giving an R.I. intermediate between that of the film and the active liquid.

The effect of using different diluents and different active liquids was studied from the ratio of the differences between the R.I. of the film and (*a*) the equilibrium R.I., and (*b*) the R.I. of the active liquid. The results are shown in Table II. in which the second column shows the equilibrium R.I. (μ) and the third column the ratio $\frac{\mu - \mu_2}{\mu_1 - \mu_2}$ where μ_1 is the R.I. of the active liquid, μ_2 of the oil film, and $\mu\mu$ the equilibrium R.I. There were used : liquid paraffin (1·480), white spirit (1·435), and linseed oil (1·484) as diluents, and bromonaphthalene (1·657), bromobenzene (1·5605), and chlorobenzene (1·5245) as active liquids, their respective refractive indices at 17° being shown in brackets.

TABLE III.—RATIO OF LINSEED OIL SORPTION TO STAND OIL SORPTION.

Active Liquid.	Diluent.		
	Paraffin.	White Spirit.	Linseed Oil.
Chlorobenzene .	1·20	1·11	1·20
Bromobenzene .	1·25	1·20	1·25
Bromonaphthalene	1·20	1·20	1·32

From Table III. it is seen that the ratios of sorption by the linseed oil and stand oil films respectively under these different conditions are approximately the same when using active liquids of similar constitution.

Ratio of the Partial Pressure of the Active Liquid to the Amount Sorbed.

The percentage composition of the active liquid in the solution in each mixture could be calculated from the R.I. values, the error between the actual and calculated volumes being less than 1 per cent. Table IV. shows a comparison between these percentage volumes and $\frac{\mu - \mu_2}{\mu_1 - \mu_2}$. For paraffin and linseed oil as diluents the ratio is approximately a constant; for white spirit as solvent, however, the ratios vary from 0·50 to 0·71. For purposes of comparison, the table includes a set of figures with chloronaphthalene as active liquid; the linseed oil film in paraffin + chloronaphthalene gave an equilibrium R.I. of 1·540.

TABLE IV.

	Percentage of Active Liquid Present.	$\frac{\mu - \mu_2}{\mu_1 - \mu_2}$.	Ratio.
Linseed oil in Paraffin — Bromonaphthalene .	41	35	0·85
Stand oil ,, ,, ,, ,, .	56	49	·87
Linseed oil in Paraffin -- Bromobenzene .	57	41	·72
Stand oil ,, ,, ,, . .	69	57	·82
Linseed oil in Paraffin — Chlorobenzene .	76	61	·80
Stand oil ,, ,, ,, . .	84	72	·85
Linseed oil in Paraffin and Chloronaphthalene	37	30	·81
Linseed oil in Linseed oil + Bromonaphthalene	26	18	·70
Stand oil ,, ,, ,, ,,	32	25	·78
Linseed oil in Linseed oil — Bromobenzene .	54	41	·76
Stand oil ,, ,, ,, ,,	58	50	·86
Linseed oil in Linseed oil + Chlorobenzene .	75	60	·80
Stand oil ,, ,, ,, .	83	72	·82

Comparing the sorption of these four active liquids with their molecular weights it will be seen that the sorbtion and the molecular weight are inversely related.

TABLE V.

	Sorption.	Molecular Weight.
Chlorobenzene .	60	94
Chloronaphthalene	30	162
Bromobenzene .	41	139
Bromonaphthalene	35	207

Influence of Negative and Positive Polarity in the Active Liquid.

The active liquids used above have a negative polarity; the figures in Table VI. were obtained with bodies of the opposite polarity.

Diffusion of the Active Liquid into the Film.

To determine whether the sorption consisted merely of the formation of a surface layer or was accompanied by diffusion, potash alum crystals (μ 1·450) were ground in linseed oil and the film given several weeks to dry. The R.I. of the crystals being below that of the film when tested by the fringe method, the film was immersed in alcohol for twenty-four hours, and the readings taken while still immersed. The R.I. of the crystals being now above that of the film, it is clear that the alcohol had diffused in and lowered the R.I. of the film throughout its mass below that of potash alum. When, however, sodium chloride crystals (μ 1·544) were ground with linseed oil and, after drying for some weeks immersed in bromonaphthalene for twenty-four hours, the R.I. of the crystals was still above that of the oil film ; bromonaphthalene does not diffuse into the film, but merely forms a surface layer.

TABLE VI.

	Equilibrium R.I.	$\frac{\mu - \mu_2}{\mu_1 - \mu_2}$.
Quinoline in Petroleum.		
Raw Linseed oil film	1·579	68
Pure Stand oil film	1·565	53
*** Ethyl Alcohol (μ 1·361) with Cedar Wood Oil (μ 1·503) as diluent.**		
Raw Linseed oil film	1·449	—
Pure Stand oil film	1·466	—
Nitrobenzene (μ 1·544) diluted with Petroleum.		
Raw Linseed oil film	1·535	67
Pure Stand oil film	1·513	25

* Amyl Alcohol and Methyl Alcohol were also more highly sorbed in the Linseed oil film, as in each case the equilibrium R.I. was lower for the Linseed oil film than for the Stand oil film.

The Probable Difference in Chemical Structure between a Raw Linseed Oil Film and a Stand Oil Film.

In order to throw further light on the difference between a film obtained from the drying of a raw oil and a film obtained by the drying of a stand oil, I obtained from Messrs. Pearson samples of the jelly formed by continuing the heating of the linseed oil in a vacuum. Portions taken from the inside of the lumps of jelly gave in liquid paraffin and bromonaphthalene an R.I. of 1·571 agreeing with the value obtained from the commercial stand oil film dried in air.

As the conversion of raw linseed oil is an endothermic process conducted in a vacuum, the polymerisation, or perhaps more correctly condensation,[1] takes place under conditions which imply that the final solid jelly is not produced by oxidation.

The close agreement between the equilibrium R.I. of this jelly and the equilibrium R.I. of a stand oil drying in the air, suggests that the " drying " of a stand oil does not involve the formation of peroxide and oxide linkages during the formation of the solid film.

The recent researches of Morrell, W. R. Davis, Rideal and Gee have thrown considerable light on the oxidation and polymerisation of the drying oils.[2] The phenomenon known as the " drying " of an oil film is evidently accompanied by the formation of peroxides taking place in the ethenoid group furthest from the carboxyl. What happens next is open to doubt, but Morrell and Davis suggest the linkage of the molecules in two different ways :—

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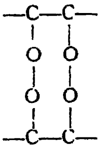
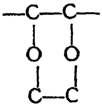
[1] H. Kurz, *Z. angew. Chem.*, 1936, **49**, 255.

[2] R. S. Morrell and H. Samuels, *J. Chem. Soc.*, 1932, 225 ; R. S. Morrell, S. Marks and H. Samuels, *J. Soc. Chem. Ind.*, 1933, **52**, 130 ; R. S. Morrell and W. R. Davis, *Trans. Faraday Soc.*, 1936, **32**, 209.

[3] Rideal and Gee, *Proc. Roy. Soc.*, *A*, **153**, 113-29 ; *Trans. Faraday Soc.*, 1930, **36**, 1 *et seq.*



and



forming an oxide.

These oxides and peroxides have a negative polarity.

In my experiments, bromo- and chlorobenzene and bromo- and chloronaphthalene which have a negative polarity were sorbed more by the stand oil than by the raw linseed oil film, and quinoline with a positive polarity was sorbed more by the raw linseed oil film. This can easily be understood if we assume a negative polarity due to the presence of peroxides or oxides, which are present in the raw linseed oil film, but absent, or nearly absent, in the stand oil film.

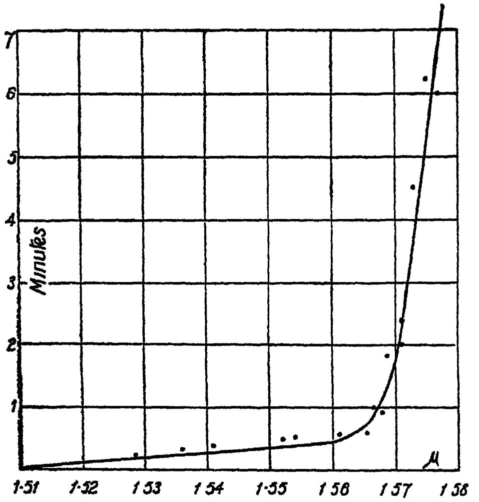


FIG. 1.—Interval between time of immersion and time of reversal of the refractive index of pure stand oil film in liquid paraffin and bromonaphthalene.

As we have seen, linseed oil can be converted to a solid by an endothermic process in a vacuum, and this solid has the same sorption for bromonaphthalene as the film formed when stand oil is dried in the air. This suggests that the "drying" of stand oil does not involve the formation of peroxides. To test this, we compared the "drying" of a sample of stand oil thoroughly washed with acetone with that of a raw oil. Approximately equal weights were spread very thinly on pieces of glass of the same area and allowed to "dry" under the same conditions. The raw oil film increased in weight 13 per cent., but the stand oil film, which dries throughout the mass, showed no appreciable increase of weight. On the other hand, a stand oil film kept in an atmosphere of coal gas did not "dry." Evidently some oxygen is necessary, possibly as catalyst when the drying takes place in the cold. It is of interest in this connection that raw linseed oil exposed to sun and air becomes a thick viscous liquid which is completely soluble in acetone, suggesting the formation of a polymer different from that found in stand oil.

Summary.

Experiments on measuring the R.I. of dry oil films by the immersion method in mixed liquids differing widely in R.I., reveal that a permanent R.I. reading is obtained at an R.I. very much above or below the R.I. of

the film, according to the R.I. of the active liquid. The explanation suggested is that there is selective sorption of one of the liquids (the "active liquid") by the film forming a surface layer having an R.I. intermediate between that of the film and the "active liquid." Experiments with various liquids reveal a wide difference between the R.I. for raw oil and stand oil films, stand oil film sorbing more of liquids of negative polarity and less of liquids of positive polarity than raw linseed oil film. A possible explanation of this is given.

In the case of active liquids of similar constitution, the ratio between the equilibrium R.I. for raw oil and for stand oil, is approximately constant, and that the ratio between the percentage present of the active liquid and the equilibrium R.I. is approximately constant.

Alcohol diffuses into the raw linseed oil film, while bromonaphthalene merely forms a surface layer.

THE VELOCITY OF CRYSTALLISATION FROM SUPERSATURATED SOLUTIONS.

By Alan Newton Campbell and Alexandra Jean Robson Campbell.

Received 22nd September, 1936.

The velocity of crystallisation from undercooled melts has been extensively studied and, if the views of Tammann are accepted, definite conclusions have been reached.[1] "For any given degree of supercooling of a substance, the velocity of crystallisation is constant. As the degree of supercooling increases, the velocity of crystallisation also increases, until at a certain temperature (about 20°-30° below the melting-point) the velocity of crystallisation attains a maximum value which is definite and characteristic for each substance. This maximum velocity remains constant over a certain range of temperature; thereafter the velocity diminishes fairly rapidly, and with sufficient supercooling, may become zero."[2] One is tempted to apply similar considerations to crystallisation from supersaturated solutions, considering degree of supersaturation as strictly analogous to degree of supercooling.

Much scattered work has also been done on velocity of crystallisation from supersaturated solutions. According to Noyes and Whitney,[3] the rate of solution (and therefore of precipitation) is determined by the rate at which solute diffuses to the surface of the growing crystal, where the concentration is that of the normally saturated solution. If this view is correct, the velocity of precipitation should comply with the formula for a unimolecular reaction, if the surface of the growing solid may be considered constant. This is found experimentally to be the case, by

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[1] Gernez, *Compt. rend.* 1882, **95**, 1278; 1884, **97**, 1298, 1366, 1433. B. Moore, *Z. physikal. Chem.*, 1893, **12**, 545. Tumlirz, *Wiener Sitzungsber. Akad.*, 1894, **103**, 11*a*, 226. Walton and Judd, *J. Physical Chem.*, 1914, **18**, 722. Hartmann, *Z. anorg. Chem.*, 1914, 88, 128. Tammann, *Z. physikal. Chem*, **23-29**. Küster, *ibid.*, **25-28**. Müller, *ibid.*, 1914, **86**, 177. Friedlander and Tammann, *ibid.* 1897, **24**, 152. Bogojawlenski, *ibid*, 1898, **27**, 585. Hasselblatt, *Z. anorg. Chem.*, 1921, **119**, 325. E. von Pickardt, *Z. physikal. Chem.*, 1902, **42**, 17. Freundlich and Oppenheimer, *Ber.*, 1925, **58**, 143.

[2] Findlay, *The Phase Rule*, 7th edit., p. 42.

[3] Noyes and Whitney, *Zeit. physik. Chem.*, 1897, **23**, 689; *J.A.C.S.*, 1897, **19**. 930.

Noyes and Whitney and by Bruner and Tolloczko.[4] In the theory of Noyes and Whitney, a layer of saturated solution is supposed always to be in immediate contact with the crystal, at least in stagnant solutions, just as in Tammann's treatment of crystallisation from supercooled melts, the temperature at the boundary of the growing crystal is supposed to be that of the melting-point, over the interval in which crystallisation velocity is constant. Unlike crystallisation from supercooled melts, however, where the intensity of the driving force, as measured by the degree of supercooling, can be kept constant, crystallisation from supersaturated solution is accompanied by a progressive decrease in the driving force, as the concentration declines. A constant velocity of crystallisation can be only expected over a small interval of time. Although the theory of Noyes and Whitney supposes the sole determining factor to be the velocity of diffusion, there must, however, in reality be another factor, namely, the velocity with which the crystal can build its units into the lattice. Theoretically at least, with increasing degree of supersaturation, there must come a time when molecules of solute are supplied to the growing crystal so rapidly that its inherent crystal building velocity, which is presumably constant, is exceeded. After this, the velocity of crystallisation would be constant, and independent of the degree of supersaturation, in strict analogy with the constant velocity of crystallisation beyond a certain degree of supercooling.

Marc [5] found that the velocity of crystallisation from very vigorously stirred supersaturated solutions, after seeding, could be slowed down and brought to a standstill, before normal solubility was attained, by addition of certain substances. His explanation of this behaviour is that the true process of crystallisation is preceded by a rapid adsorption of solute molecules on the surface of the inoculating solid, the subsequent relatively slow process being the arrangement of these molecules in the orm of the crystal lattice. The slowing down or inhibition of the crystallisation process by addition of certain anticatalysts is due to their adsorption and displacement of solute molecules from the surface of the crystalline seed. If this view is correct, there are three links in the chain of crystal growth, *viz.*, diffusion, establishment of the adsorbed layer, and actual crystal growth.

Apart from velocity of crystallisation from a pure solution, there remains the interesting question of the effect of foreign additions to the solution. Such additions may affect either the solution or the solid. From the point of view of the diffusion theory, it would be expected that additions which increase the viscosity of the solution, would decrease the velocity of crystallisation. According to Marc, additions which were adsorbed by the solid phase decreased the velocity of crystallisation. On the whole, one would expect the velocity of crystallisation to be greatest from pure solution.

In all work on velocity of crystallisation, whether from supercooled melts or from supersaturated solutions, the tendency towards spontaneous crystallisation must be taken into account. If nuclei are being formed spontaneously, the observed velocity on inoculation will appear greater than the truth. Much less work, and none of it quantitative, has been done on the nuclear number (number of spontaneously formed nuclei per unit of volume per unit of time) of supersaturated solutions. According to von Weimarn,[6] lowering the surface tension, or increasing the association of the solute increases the number of crystallisation centres. The protective action of lyophile colloids in inhibiting precipitation is well known.[7] The usual view taken is that the nuclei aggregate to the size of suspensoid particles, and that these are then protected by adsorption of a layer of emulsoid.

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[4] Bruner and Tolloczko, *Z physik Chem*, 1900, **35**, 283; *Z. anorg. Chem.*, 1901, **28**, 314; 1903, **35**, 23; 1903, **37**, 455.

[5] Marc, *Z. physikal. Chem*, 1908, **61**, 385; 1909, **67**, 470; 1909, **68**, 104; 1911, **73**, 685; 1911, **75**, 710; 1912, **79**, 71.

The object of the present work was an extended experimental investigation of the whole subject, taking into account:

1. Nuclear number or tendency to spontaneous crystallisation.
2. Velocity of crystallisation in inoculated (stagnant) solutions, in the absence of spontaneous crystallisation. It was desirable to push these measurements to as high a degree of supersaturation as possible, in order to discover any tendency of the velocity to attain a maximum.
3. The effect of addition agents on the above phenomena, such additions being chosen as would markedly affect viscosity or surface tension.
4. The effect of colloidal additions.

We endeavoured to introduce a more quantitative aspect into the work than has perhaps hitherto been the case.

Experimental.

The substance chosen for study was barium succinate, since its solubility is appreciable, but not large. The method consisted in mixing solutions of barium chloride and of sodium succinate, such as to give a required degree of supersaturation, and measuring the conductivity at intervals of time. The temperature was 25° throughout. In the experiments on velocity of crystallisation, the solution, which was always 100 c.c. in volume, was inoculated after mixing with one gram of finely crystalline barium succinate. (The same preparation was used throughout.) In this way the inoculating surface would be constant.

The first experiments dealt with the question of spontaneous crystallisation, that is, the time after mixing before the appearance of visible crystals or the observance of a decrease in conductivity. The obvious precautions against chance inoculation were taken. Crystals were usually observed before a marked decrease in conductivity could be detected. It might be thought that this interval of time would be a matter of chance, and therefore variable, but this was not found to be the case. No doubt the nuclear number is large and constant but the nuclei are not actually detected until they have grown to an appreciable size, so that the observed stability is affected not only by the nuclear number, but by the velocity of crystallisation. Still, so long as no spontaneous fall of conductivity occurred within one hour after mixing, it was safe to conduct measurements on velocity of inoculated crystallisation, since this velocity was such as to carry the concentration well below the value at which, within one hour, spontaneous crystallisation might occur.

The investigations of crystallisation from pure solutions were followed by similar measurements on solutions containing glucose to increase the viscosity, alcohol to lower the surface tension, and agar-agar to observe the protective effect. Viscosity was measured with an Ostwald viscometer, a method which does not appear to give satisfactory results with colloidal solutions, since the time of flow increased with the ageing of the gel. In any case, since a gel is heterogeneous, the viscosity could have no precise significance. Similar anomalous results were obtained with the surface tension of the agar-solution, which was determined both by capillary rise and by the stalagmometer. Possible adsorption on barium succinate crystals was investigated by stirring 100 c.c. of solution with one gram of barium succinate powder, and determining the concentration of solute, before and after, by suitable analytical means, *e.g.*, the glucose was determined polarimetrically.

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[6] von Weimarn, *Kolloid Z.*, 1909, **27**, 4.

[7] Freundlich, *Colloid and Capillary Chemistry*, 1922 edit., p. 596.

The barium chloride ($BaCl_2 . 2H_2O$) used was Mallinckrodt's "pure crystals." Sodium succinate was prepared by neutralisation of Baker's C.P. succinic acid with the calculated quantity of stick sodium hydroxide. The preparation was dehydrated at 100°. Barium succinate was prepared by precipitation from mixed solutions of barium chloride and sodium succinate, and dried at 110°. It was found to contain 52·96 per cent. Ba (calc. for anhydrous $Ba . C_4H_4O_4 = 54{\cdot}15$ per cent.). The sodium succinate contained 28·32 per cent. Na (calc. for anhydrous $Na_2C_4H_4O_4 = 28{\cdot}40$ per cent.).

TABLE I.—SOLUBILITY AND CONDUCTIVITY OF BARIUM SUCCINATE IN VARIOUS MEDIA.

Solvent.	Solubility (grams. per 100 grs. Solvent).	Specific Conductivity.	Molar Conductivity.†
Distilled water (sp. cond. = $9{\cdot}0 \times 10^{-5}$ mhos.	0·398	$2{\cdot}22 \times 10^{-3}$ mhos.	142·0
10 per cent. glucose	0·420	$1{\cdot}52 \times 10^{-3}$ mhos.	98·0
20 ,, ,,	0·440	$1{\cdot}20 \times 10^{-3}$ mhos.	80·5
40 ,, ,,	0·425	$0{\cdot}36 \times 10^{-3}$ mhos.	30·2
10 per cent. alcohol (by volume)	0·235	$0{\cdot}902 \times 10^{-3}$ mhos.	100·0
20 ,, ,, ,,	0·088	$0{\cdot}413 \times 10^{-3}$ mhos.	122·0
40 ,, ,, ,,	Practically insoluble.	$0{\cdot}056 \times 10^{-3}$ mhos.	—
0·02 per cent agar-agar	0·354	—	—
0·1 ,, ,,	0·325	—	—
*0·20 ,, ,,	0·282	—	—
0·2 ,, ,,	—	$2{\cdot}11 \times 10^{-3}$ mhos.	191·0
1·7 ,, ,,	—	$1{\cdot}69 \times 10^{-3}$ mhos.	
1·4 ,, ,,	—	$1{\cdot}78 \times 10^{-3}$ mhos.	
1·0 ,, ,,	—	$1{\cdot}36 \times 10^{-3}$ mhos.	

* The solubility in higher concentrations of agar-agar could not be obtained, as the solutions were unfilterable, even under suction.

† A rough value of μ_∞ for barium succinate can be obtained by taking l_c for $\frac{1}{2}$Ba = 55 at 18° C. (Int. Crit. Tables, Vol. 6, p. 230), $\frac{1}{\Lambda}\left(\frac{d\Lambda}{dT}\right)_{18^\circ} = 0{\cdot}0239$, and l_a for $\frac{1}{2}C_4H_4O_4 = 25$ (a pure guess), as μ_∞ $Ba\ C_4H_4O_4 = 178$.

Conductivity was determined in the usual way, without special precautions. The distilled water used had a high conductivity, $9{\cdot}0 \times 10^{-5}$ mhos., but it was not found necessary to take this into account, except in the determination of the cell constant, and of the molar conductivity of sodium chloride, in the more dilute solutions.

To evaluate the true degree of supersaturation, it was necessary to know the normal solubility of barium succinate in various media, and these determinations were carried out. It was also thought that the degree of supersaturation could be evaluated from the conductivity, and for this purpose the conductivities of the various media saturated with barium succinate were determined. For this purpose also it was necessary to know the specific conductivity of sodium chloride solutions, of different molarities. The figures for water were taken from International Critical Tables, but for other media, the data were obtained experimentally, using the ordinary technique. No high degree of accuracy is therefore attained, particularly in the more dilute solutions.

As these preliminary data are required in all that follows, the solubility of barium succinate and the conductivities of saturated solutions of barium suscinate, in various media, are given in Table I. Table II. contains the conductivities of sodium chloride.

TABLE II.—CONDUCTIVITIES OF SODIUM CHLORIDE IN VARIOUS MEDIA.*

Dilution in Litres.	Concentration in Mols./Litres.	10 Per Cent. Glucose Sp. Cond.		20 Per Cent. Glucose Sp. Cond.		40 Per Cent. Glucose Sp. Cond.		10 Per Cent. Alcohol Sp. Cond.		20 Per Cent. Alcohol (by volume) Sp. Cond.		40 Per Cent. Alcohol (by volume Sp. Cond.	
		× 10³.	μ_v.	× 10³	μ_v	× 10³.	μ_v.	× 10³.	μ_v.	× 10³.	μ_v.	× 10³.	μ_v.
1	1 000	72·5	72·5	54·75	54·75	33·6	33·6	68·5	68·5	53·0	53·0	35·0	35·0
2	0·500	38·00	76·0	31·00	62·00	18·8	37·6	36·5	73·0	28·5	57·0	19·2	38·4
4	0·250	20·70	82·8	17·00	68·00	10·25	41·0	20·3	81·2	15·3	61·2	10·1	40·4
8	0·125	11·24	90·0	9·11	73·00	5·45	43·6	10·7	85·6	7·9	62·2	5·65	45·2
16	0·063	5·79	93·0	4·81	77·00	2·85	45·6	5·75	92·0	4·3	69·0	3·27	51·8
32	0·031	3·04	97·5	2·49	80·00	1·42	45·6	3·27	105·0	2·26	72·5	1·64	52·5
64	0·016	1·61	103·0	1·32	84·50	0·714	45·8	1·71	108·0	1·51	77·5	0·85	54·5
128	0·008	0·81	104·0	0·73	92·50	0·367	46·8	0·88	112·0	0·66	85·0	0·43	54·5
256	0·004	0·42	108·5	0·41	104·00	0·183	47·0	0·46	116·0	0·36	92·0	0·23	58·5
512	0·002	0·22	113·0	0·21	107·00	0·087	44·7	0·23	116·0	0·24	121·0	0·11	57·5
Solvent alone		0·056	—	0·040	—	0·051	—	0·034	—	0·037	—	0·030	—

* All conductivities corrected for conductivity ot solvent.

The conductivities in agar solution were also determined but, owing to the high conductivity of the agar itself, the figures were irregular. They served, however, to illustrate the known fact that conductivities in gels are much the same as in water.

Spontaneous Crystallisation.

Table III. shows the times from mixing up to the first detection of crystals, either detected visibly or by a fall in conductivity.

A consideration of Table III. shows that while the limit of complete stability, as determined by the non-appearance of crystals in twenty-four hours, is not greatly raised by the addition of glucose, a much greater degree of super-saturation is necessary, with increasing concentration of glucose, to produce immediate crystallisation. Glucose greatly increases the viscosity while hardly affecting the surface tension. It seems to us, from the subsequent experiments on velocity of crystallisation, that the effect is purely to be attributed to the decreased velocity of crystallisation; in other words, the nuclear number is not affected, but the microscopic or submicroscopic nuclei take a longer time to grow to detectable size.

Allowing for the decreased solubility of barium succinate in alcoholic solutions, and for the decrease in velocity of crystallisation, due to increased viscosity, it appears that, if anything, the nuclear number is slightly raised by lowering the surface tension, as von Weimarn suggests.

The effect of the additions of agar is what might have been expected. Even so small an amount as 0·02 per cent. exerts a stabilising effect. On the other hand, even with 1 per cent. agar, the stabilisation is not permanent in the higher regions of supersaturation, *e.g.*, 1000 per cent. No doubt the nuclei first formed are enveloped and protected, but as the process of formation of nuclei goes on, the colloid must be eventually used up. That it is used up shows how high the nuclear number must be in a solution of 1000 per cent. supersaturation.

TABLE III.—SPONTANEOUS CRYSTALLISATION.

Degree of Supersaturation Per Cent.	Time in Hours to Detection of Crystals.
Solvent Water.	
10	> 48
20	> 72
40	> 24
80	> 24
100	= 21
200	> 1
400	= 0·28
300	= 1·85
200	= 2·35
Solvent 10 % Glucose.	
100	> 48
200	= 24
300	> 1·5
400	= 0·6
Solvent 20 % Glucose.	
208	= 24
Solvent 40 % Glucose.	
260	= 24
390	= 24
520	= 24
650	= 3
780	= 0·8
900	= 0·9
Solvent 10 % Alcohol (vol.).	
173	= 24
347	= 0·9
520	= 0·3
695	= 0·00
Solvent 20 % Alcohol (vol.).	
460	= 2·25
920	= 0·00
Solvent 40 % Alcohol (vol.).	
*Very Large	= 0·00
* ,, ,,	= 0·00
* ,, ,,	= 0·00
* ,, ,,	= 0·00
Solvent 0·1 % Agar.	
100	> 24
200	> 24
400	= 24
500	= 24
700	= 1·0
Solvent 0·5 % Agar.	
500	= 1·5
Solvent 0·2 % Agar.	
400	= 0·5
Solvent 0·2 % Agar.	
700	= 4·0
1000	= 0·5
1000	= 0·7
Solvent 0·40 % Agar.	
1000	= 1·25
Solvent 1·0 % Agar.	
1000	= 2·4
1500	= 0·00

* Made up to represent 100 per cent., 50 per cent., 20 per cent. and 10 per cent. supersaturation in pure water respectively.

Velocity of Inoculated Crystallisation.

With reference to the view of Noyes and Whitney[3] that the process of crystallisation is purely one of diffusion, there are collected in Table V. some of the results of these measurements, the constant of a unimolecular reaction being calculated from the formula :—

$$k' = \frac{1}{t}\log_{10}\frac{k_0 - k_\infty}{k_t - k_\infty}$$

where, k_0 = Specific conductivity at start
k_∞ = ,, ,, ,, end
k_t = ,, ,, ,, time t (in hours).

It should be borne in mind, however, that barium succinate is an ionised solute, perhaps completely ionised. We therefore have in normally saturated solution :

$$\begin{aligned}[\mathrm{Ba\,C_4H_4O_4}]_1 &= k[\mathrm{Ba}^{++}] \times [\mathrm{C_4H_4O_4}^{--}] \\ &= kc_1^2\end{aligned}$$

TABLE IV.—VISCOSITY AND SURFACE TENSION.

Solution.	Relative Viscosity (Water = 1·000).	Relative Surface Tension (Water = 1·000).
Distilled Water, saturated with $BaC_4H_4O_4$.	1·01	—
$BaCl_2 + Na_2C_4H_4O_4$. 10 per cent. Supersat.	1·015	—
$BaCl_2 + Na_2C_4H_4O_4$ 20 per cent. Supersat.	1·02	—
Solutions of $BaCl_2$ and $Na_2C_4H_4O_4$ in water.	—	But little different from water.
$BaCl_2 + Na_2C_4H_4O_4$. 80 per cent. Supersat.	1·02	—
$BaCl_2 + Na_2C_4H_4O_4$. 100 per cent Supersat.	1·03	—
$BaCl_2 + Na_2C_4H_4O_4$. 200 per cent. Supersat.	1·015	—
$BaCl_2 + Na_2C_4H_4O_4$. 300 per cent. Supersat.	1·022	—
10 per cent. Glucose	1·20	0·975
20 per cent. Glucose	1·43	1·045
40 per cent. Glucose	2·80	1·015
* 10 per cent. Alcohol (by volume) . .	1·12	0·680
20 per cent. Alcohol ,, . .	1·41	0·57
40 per cent. Alcohol ,, . .	1·86	0·51
0·1 per cent. Agar	>2 (increasing with age of gel).	0·88
0·05 per cent. Agar	1·30	0·91
0·02 per cent. Agar	1·11	0·91
0·2 per cent. Agar	>6·0	Unsatisfactory for this and higher concentions.

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* Highly impure commercial alcohol, which could not be purified by distillation.

while in a solution, supersaturated n times, we have

$$\begin{aligned}[\mathrm{Ba\,C_4H_4O_4}]_2 &= k \times n\,c_1 \times n\,c_1 \\ &= kn^2c_1^2\end{aligned}$$

$$\therefore \frac{[\mathrm{Ba\,C_4H_4O_4}]_2}{[\mathrm{Ba\,C_4H_4O_4}]_1} = \frac{kn^2c_1^2}{kc_1^2} = n^2.$$

It therefore appears that the expression for the velocity constant should be

$$\begin{aligned}k'' &= \frac{1}{t}\log_{10}\frac{a^2}{a^2 - x^2} \\ &= \frac{1}{t}\left(\log_{10}\frac{a}{a - x} + \log_{10}\frac{a}{a + x}\right)\end{aligned}$$

i.e., k'' is obtained from k', the "ordinary" expression for the constant of a unimolecular reaction, by adding to it the expression $\frac{1}{t}\log_{10}\frac{a}{a+x}$, *i.e.*, a negative correction.

Examination of Table V. shows: (1) the values of k' are not constant, but show, without exception, a pronounced drift with time from high to low values; (2) The values of k'' are more nearly constant, but they also

TABLE V.—VELOCITY OF CRYSTALLISATION.

Degree of Supersat. Per Cent.	Solvent.	Time in Hours.	Sp. Conduc. × 10^3.	k'.	k''.
150	Water.	0	12·1	—	—
		0·1	11·7	0·800	0·21
		0·3	11·6	0·343	0·07
		0·9	11·4	0·169	0·07
		1·2	11·3	0·146	0·05
		1·3	11·2	0·150	0·04
		1·6	11·1	0·148	0·06
		∞	9·7	—	—
300	Water.	0	17·9	—	—
		0·1	17·3	0·70	0·10
		0·3	17·0	0·37	0·11
		0·5	16·8	0·28	0·08
		0·6	16·6	0·27	0·06
		1·0	16·3	0·21	0·07
		1·3	15·8	0·24	0·11
		∞	13·7	—	—
400	10 % Glucose	0	18·4	—	—
		0·1	16·3	2·15	0·95
		0·4	15·9	0·69	0·29
		0·6	15·7	0·51	0·22
		0·8	15·6	0·40	0·18
		1·0	15·4	0·355	0·17
		1·3	14·7	0·385	0·29
		1·6	14·5	0·345	0·26
		∞	13·0	—	—
650	40 % Glucose	0	10·50	—	—
		0·2	9·20	1·35	0·55
		0·4	8·95	0·75	0·25
		0·6	8·80	0·70	0·35
		1·0	8·75	0·43	0·22
		2·4	8·55	0·22	0·12
		∞	7·70	—	—

Degree of Supersat. Per Cent.	Solvent.	Time in Hours.	Sp. Conduc. × 10^3.	k'.	k''.
520	10 % Alcohol	0	12·5	—	—
		0·4	11·1	0·85	0·40
		0·9	10·7	0·56	0·30
		1·0	10·6	0·57	0·24
		2·7	10·4	0·27	0·17
		6·0	9·9	—	—
		∞	9·9	—	—
460	20 % Alcohol	0	6·45	—	—
		0·05	5·40	6·80	1·20
		0·10	5·20	4·44	2·24
		0·20	5·10	2·50	1·35
		0·80	5·00	0·74	0·44
		3·00	4·90	0·23	0·15
		∞	4·50	—	—
500	0·1 % Agar .	0	26·2	—	—
		0·3	22·7	0·99	0·56
		0·7	21·7	0·65	0·34
		1·0	20·4	0·80	0·54
		1·6	20·1	0·58	0·35
		∞	19·3	—	—
1500	1·0 % Agar	0	64·5	—	—
		0·05	61·5	3·20	0·40
		0·15	60·5	1·46	0·54
		0·3	58·0	1·52	0·80
		∞	54·5	—	—

show the drift, to a less extent; (3) The results in agar solution are irregular, as is perhaps to be expected; the inoculating solid will be more or less haphazardly protected.

The drift in both the k values rules out the theory of diffusion as a complete explanation of the mechanism of crystallisation, but the fact that the drift is much less with k'' indicates that the process is largely one of diffusion, as is no doubt the case. The fundamental assumption of Noyes and Whitley is that the concentration at one end of the diffusion layer, the face of the growing crystal, is constant and equal to that of a normally saturated solution. The behaviour of the k values indicates that the reaction is at first faster and subsequently slower than this mechanism requires. It seems to us that the view of Marc might very well be incorporated here, *viz.*, that the surface of the growing crystal is covered with an adsorbed layer in which the concentration is higher than that of normal saturation. In accordance with the adsorption isotherm, the concentration in this layer would depend on the concentration in solution, but in such a way that it was relatively greater from the more dilute solutions, and this would account for the slowing down of the diffusion process with the passage of time. Of course, this view requires a velocity of crystal building comparable with the velocity of establishment of the adsorbed layer, but there is no *a priori* reason why the velocity of crystal building should be inordinately great. Indeed, it may even vary with the concentration in the adsorbed layer.

TABLE VI.—EFFECT OF ADDITION AGENTS ON VELOCITY OF CRYSTALLISATION.

— dc/dt = Fall in Sp. Cond. during 1st hour × 10^3.

*Degree of Supersaturation Per Cent.	Solvent.	Water.	Glucose.			Alcohol.			Agar
			10 Per Cent.	20 Per Cent.	40 Per Cent.	10 Per Cent.	20 Per Cent.	40 Per Cent.	
10	*400*	0·10	*5·5*		*0·45*				*7·3* (0·02) %) *2·1* (0·10 %).
20	*500*	0·10			*0·65*	*1·90*	*1·45*		*2·8* (0·05 %).
40		0·15							
80	*700*	0·25			*1·05*	*3·20*			
100	*800*	0·40	0·30		*1·25*				(*4·8* (0·1 %).
150	*900*	0·70			*1·40*		*2·05*		
200	*1000*	1·40	0·70	0·30		0·95			*6·2* (0·2 %).
250	*1500*	2·20			0·25				*10·0* (1·0 %).
300	Very high.	3·20	*2·1*			1·75		{*14·2*, 4·05, *2·06*	

* For purposes of comparison, with glucose and alcohol solutions, where the solubility varies, the degree of supersaturation is given as that of the nearest water supersaturation.

Table VI. shows the effect of the addition agents by giving the fall in specific conductivity during the first hour after inoculation, together with the degree of supersaturation and the solvent. The figures in italics correspond to the higher degrees of supersaturation indicated. The concentrations of the solvents are indicated at the head of the table, except in the case of agar, where the concentration appears in brackets after the relevant value of dc/dt.

Glucose and to a less extent alcohol, slow down velocity of crystallisation. It seems, then, that viscosity of the medium is the major factor in determining velocity of crystallisation. Since, however, alcohol increases the viscosity almost as much as glucose, without proportionately decreasing the crystallisation velocity, it may be that reduced surface tension has an effect in the opposite direction, and this may be connected with the existence of an adsorbed layer. The results with agar-agar are anomalous, and not all are included in the table. Probably the presence of agar-agar is without effect on the true velocity of crystallisation, while exerting a pronounced protective effect on spontaneous crystallisation.

Diffusion Experiments.

An approximate measurement of the relative rates of diffusion in the different media was obtained by placing one gram of each of the substances concerned in the precipitation equation in a dry test tube, carefully pouring in solvent and inserting a pair of conductivity electrodes. This apparatus was kept in the thermostat at 25° and measurements of conductivity taken from time to time. In Table VII. the increase in specific conductivity during the first fifty hours is given, together with the nature of the solute and solvent. The velocity of diffusion is slowed down in inverse proportion to the viscosity and direct proportion to the decrease in velocity of crystallisation, so that the latter must be largely a process of diffusion, as it obviously is.

TABLE VII.—Relative Velocities of Diffusion.

Increase in Specific Conductivity during first *50 hours*, in mhos. 10^3

Substance.	Solvent.						
	H_2O	10 Per Cent. Glucose.	20 Per Cent. Glucose.	40 Per Cent. Glucose.	10 Per Cent. Alcohol.	20 Per Cent. Alcohol.	40 Per Cent. Alcohol.
$BaCl_2 . 2H_2O$	16·2	3·5	1·81	—	2·85	3·9	—
$Na_2C_4H_4O_4$	5·1	0·8	—	—	3·55	—	—
$NaCl$ . .	33·4	12·9	12·0	2·0	21·0	12·2	2·6
$BaC_4H_4O_4$.	0·175	—	—	—	—	—	—

Adsorption Experiments.

None of the adsorption experiments showed any effect. It appears that neither barium succinate in solution, nor any of the addition agents are adsorbed to any appreciable extent.

Summary.

Using supersaturated solutions of barium succinate, we have studied the following phenomena:

1. Tendency towards spontaneous crystallisation.
2. The velocity of crystallisation after inoculation with a constant weight of inoculant. The velocity increased with degree of supersaturation, and showed no tendency to approach a maximum up to 1500 per cent. supersaturation. The values of the velocity "constants" lead us to modify somewhat the diffusion hypothesis of Noyes and Whitney.
3. The velocity of crystallisation is shown to be decreased by increasing the viscosity of the medium, and probably increased by lowering the surface tension.
4. The protective action of a colloidal addition (agar) has been examined quantitatively.

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THE APPLICATION OF THE LOGARITHMIC SECTOR TO CORROSION PROBLEMS.

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This paper forms part of a thesis approved for the degree of Doctor of Philosophy in the University of London. It describes experiments aimed at applying the logarithmic sector method of spectrographic analysis, as developed by Twyman and Simeon,[1] to certain chemical estimations associated with a study of the corrosion of metals in liquids. It was sought to estimate very small quantities of the metals in solution, and the work therefore follows on that of Twyman and Hitchen [2] on the use of the log sector with solutions. The photometric aspect of the use of the log sector has been examined by several investigators, including Martin, Burke and Knowles,[3] and in the present paper it will be shown that the possibility of extending the method to micro-analysis depends on the extent to which improvements can be made in this direction.

Apparatus.

The apparatus consisted of a high-tension electrical equipment, an apparatus for sparking the solutions, a Hilger medium quartz spectrograph (E 3), a Hilger logarithmic sector (H. 232), and an arrangement for measuring the lengths of lines on the spectrograms.

The sparking apparatus was a development of that devised by Twyman and Hitchen, modified so as to be capable of the routine analysis of very small volumes of solution. The estimation of traces of metals calls for a method which requires only a minimum of material for analysis. Experiments on the effect of reducing the rate of flow of solution to the spark showed that while the intensities were unaltered down to about 10 c.c./min., the spark tended to pass down the quartz capillary tube with slower rates of flow, causing instability of the liquid meniscus, and a violent irregular discharge.

It will be shown, on the other hand, that the solution is unchanged for practical purposes by its passage through the spark gap, and may therefore be used many times over. Hence, although the rate of flow has to be kept at about 30 c.c./min. to maintain the stability of the spark, it is yet possible to make an estimation with quite a small volume of solution. The apparatus sketched in Fig. 1 shows how this can be accomplished by the continuous circulation of as little as 20 c.c. through the spark gap.

The solution flows from the reservoir A to the quartz capillary tube B, where it flows up round the gold wire C. The spark passes between the surface of the solution and the graphite rod D. The spark is entirely surrounded by the glass screen E, and a quartz window F allows the radiation through. Fumes are sucked away through the side tube G, and the screen E is high enough to prevent any splashes or spray from being projected out at the top and causing damage to the spectrograph.

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[1] Twyman and Simeon, *Trans. Opt. Soc.*, 1929-30, **31**, 169.

[2] Twyman and Hitchen, *Proc Roy. Soc.*, *A* , 1931, **133**, 72.

[3] Martin, Burke and Knowles, *Trans. Faraday Soc.*, 1935, **31**, 495.

Used solution flows out at H and makes a head in the left limb of the U tube which more than counterbalances the aerated column in the right limb. The latter, therefore, ascends and carries the solution back to the reservoir. The U-tube or " air lift " is surrounded by a mixture of ice and water to cool the solution back to its starting temperature. Air is injected into the right limb by means of the two aspirators shown.

To prevent the accumulation of liquid from previous estimations at the points of entry and exit, tubes J and K were provided. By allowing a little solution to flow out at J and K before an analysis, the circulating liquid is separated by a column of its own composition from possible " dead ends." A filter pump is connected on at L, and fumes condensing in the tube run back into the water seal N. A supply of distilled water connected on at M enables the whole apparatus to be washed out *in situ* through O and G without disturbing the focus.

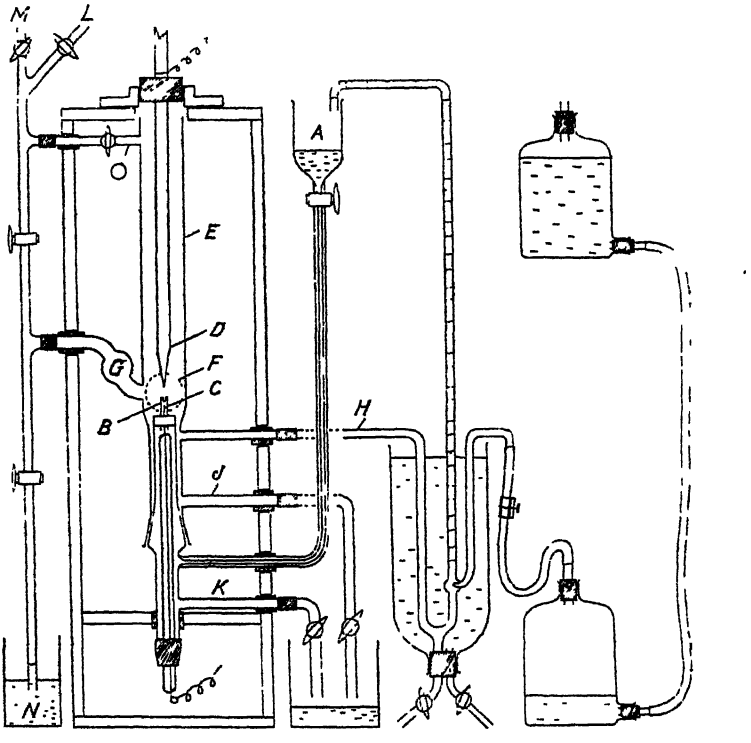

Fig. 1.

Experiments on the sharpness of the upper carbon electrode showed that increasing the sharpness of the point increased the intensity of every line in the spectrum of the spark radiation, the ratio of the intensities remaining unaltered. The exact degree of sharpness is therefore immaterial, and visual control was found to be sufficient. Since the potential across the spark gap depends on the gap width, an objective and eyepiece were permanently mounted so as to be focussed on the gap. By means of a scale in the eyepiece, the gap width was set at 3 mm. before each exposure, and this increased to about 4·5 mm. after sparking, owing to erosion of the graphite.

It was found that the temperature of the solution fed to the spark had no effect between 10° C. and 30° C. In practice, the solution in the reservoir was kept at about 18° C., a rise of 5° C. occurring on passing through the spark. If the temperature is allowed to get too high, fuming of the acid electrolyte eccurs. The rate of fume removal was found to be immaterial over the range 800 c.c./min. to 4000 c.c./min. examined. Very low rates of fume removal are to be avoided on account of the formation of a vapour cloud round the spark, and consequent absorption.

Electrical System.

After unsuccessful trials of a mercury interrupter and induction coil, the best electrical system was found to be that shown in Fig. 2, the high-tension voltage being produced by a transformer working off A.C. mains. Devices for controlling the oscillations in the secondary circuit, such as those recommended by Feussner, were considered unsuitable for the present work on account of the loss of spark intensity which they are bound to cause. No auxiliary spark gap in series with the sparking apparatus was used, since it was found to have little effect on the quality or constancy of the resulting radiation. The magnitude of each of the electrical factors was very carefully examined, in order to suppress, as far as possible, the background intensity with respect to the line intensity. This is clearly of paramount importance where very weak lines are concerned, and the increased sensitivity of the present work is partly due to improvements in this direction. The values of 2 millihenries inductance and 0·012 microfarad capacity are therefore rather greater than those used by most previous workers. The exact secondary voltage on open circuit is unknown, but was of the order of 7000 volts. The current across the gap was the greatest consistent with the stability of the spark. Calibrated Leyden jars were used to supply the capacity, but their use is strongly to be deprecated on account of their inconstancy and liability to puncture.

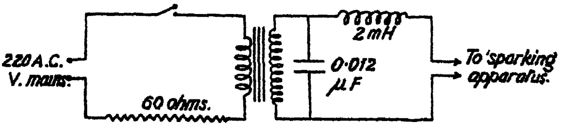

FIG. 2.

Optical System.

The optical arrangement follows, with some modifications, that laid down by Twyman and Simeon,[1] depending on the principle that every ray passing through the slit must pass unhindered to the appropriate image on the photographic plate. As shown in Fig. 3, an image of the spark A is projected by the quartz lens B into the plane D of the collimator. The quartz lens B was placed close to the slit in order to obtain as large an area of uniform illumination as possible, and was mounted in a projection of the sparking apparatus box, in order to reduce the number of focussing variables.

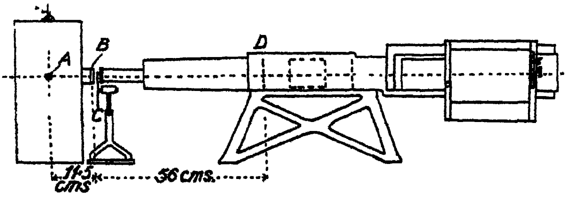

FIG. 3.

The spark A was as close as possible to the lens B, the limit being set by the size of the spark image, which must be wholly contained within the aperture of the collimator D. Decreasing the distance from the spark to the condensing lens, decreases the exposure time, so that a decrease in the collimating distance of the spectrograph enables a higher sensitivity of the method to be attained. Some advance in the estimation of very weak solutions might possibly be made along these lines in the future, by enabling analyses to be made with shorter exposures on smaller volumes of solution.

The above considerations fixed definite optimum values for the focussing distances, as marked in the diagram, and a special quartz lens with the appropriate focal length was ground in the optics workshop of the Royal College of Science. The sector C was mounted within 2 mm. of the slit to avoid any " scaling down " of sector lengths by the converging beam, and to ensure that a sharp shadow was thrown. The speed of rotation of the sector was 250 to 300 r.p.m. Too high a rate of rotation is to be avoided on account of the vibration produced.

The theory of the sector exposures has been described by Twyman and Simeon,[1] and some developments, partly based on the present work, have been made by Martin, Burke and Knowles,[3] including a discussion on the question of errors in the figuring of the sector periphery, and the means of correction. For the present work an accurate sector was made with smaller peripheral errors, and the question of corrections did not arise. The difference between the errors at any two points did not exceed 0·1 mm., except for very long lines. The slit width used was 0·08 mm., this being found to give the best type of line end-point, and the best ratio of line intensity to background intensity according to the principle described in the paper by Martin, Burke and Knowles.

Photographic Aspect.

From the photographic and photometric points of view, this research presented new problems peculiar to the use of very weak intensities, and upon their solution depends the degree of success of all such micro-estimations. Owing to the complexity of the spectra of the metals iron, nickel, chromium and manganese involved in this work, and the rather insufficient dispersion of the medium quartz spectrograph, it was found necessary to work in the ultra-violet region only. A fast " ordinary " plate had thus to be used, and Ilford Monarch plates were found to be most satisfactory. A spectrograph with a greater dispersion might enable the extremely fast modern Panchromatic plates to be employed, thus increasing the sensitivity of the method. Exposures of 5 minutes' duration were employed in all cases.

The difficulty of measuring the lengths of lines on such fast plates has been explained by Martin, Burke and Knowles, and tends to diminish greatly the accuracy of the method. The lack of definition at the end-point is, however, partly overcome by using a very contrasty developer. In the present work development was carried out in caustic hydroquinone at 18° C. for two minutes in an open dish with gentle rocking.

Careful experiments showed that neither varying the time of development between 2 and 4 minutes, nor altering the development temperature between 15° C. and 25° C. had any definite effect on the difference in line-lengths. This perhaps explains why Twyman and Fitch[4] found no improvement resulting from a much more carefully controlled system of development. More than 3 minutes' development, or a higher temperature than 20° C., however, produce fogging which is very detrimental to line measurement, and for this reason the values mentioned in the last paragraph were adopted.

The effect on the end-points of fogging due to extraneous light is shown in Fig. 4. As shown by Martin, Burke and Knowles, the log exposure axis in the characteristic curve of an emulsion can be replaced by a scale of

[4] Twyman and Fitch, *J. Iron and Steel Inst.*, 1930, **122**, 289.

line-lengths, approximately 5 mm. taking the place of an unit change in log E. In this way a curve is obtained showing the gradation of density along a line, and particularly the form of the end-point. The lower curve in Fig. 4 is the characteristic curve of the Monarch emulsion.

The upper curve was obtained by adding to every point on the line an arbitrary exposure of 0·006 units, on the same scale as the axis of abcissae, and finding the resulting density from the lower curve. If we assume that fogging is caused by the addition of a constant small increment of exposure to every point on the plate, the upper curve thus represents the gradation of density on a fogged plate. This particular value of extra exposure was chosen because it approximately doubled the overall fogging on the plate, and thus gave a fair representation of what might occur in practice.

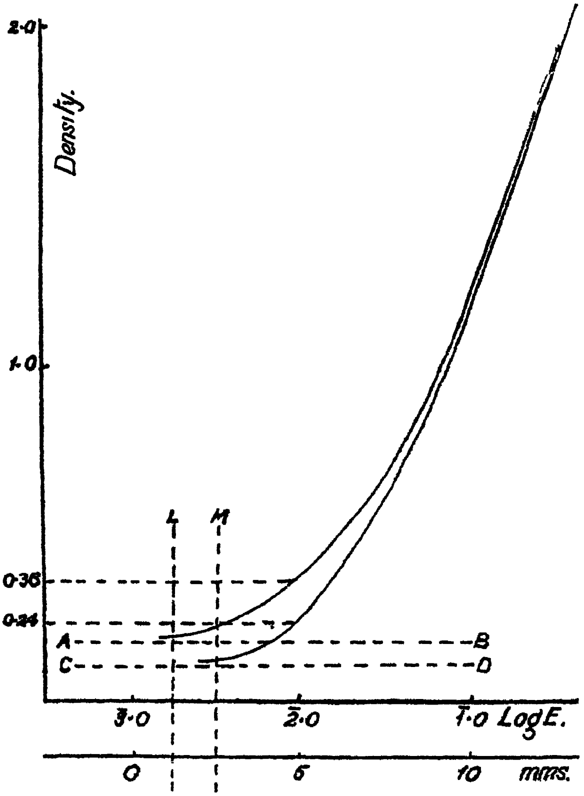

Fig. 4.

The form of the end-point in both cases is practically the same, the fogged line being about 1 mm. longer, since the end-point has moved from M to L. With regard to the density of the surrounding plate, however, namely AB and CD, there is less percentage increase at a given distance to the right of L on the "fogged" curve than there is at the same distance to the right of M on the lower curve. This makes the end-point determination much more difficult on the fogged plate.

These deductions are borne out in practice, and the utmost care has to be taken to prevent fogging. It may be remarked, though, that the increase in length is of no consequence, since it affects both of the spectrum lines whose difference in length is being measured to an equal extent.

The cutting of the plates into strips, loading of slides, and development were all carried out in complete darkness, since such a procedure was found to be necessary to minimise fogging.

Some previous workers have advocated "cutting" the plates with potassium ferricyanide, claiming that the reduction process improved the sharpness of the end-points. The writer, however, can find little to commend this procedure with fast plates, no improvement in the end-points being observed, whilst the low density gradient at the ends of the lines led to large and irregular lengths of line being removed by the chemical action.

In this connection a theoretical conception of some interest is put forward in Figs. 5*a* and 5*b*. Fig. 5*a* represents an example of the action of a weak solution of potassium ferricyanide with hypo on various densities,[5] a larger percentage of the total silver being removed from the less dense areas. Curve 1 in Fig. 5*b* is the ordinary characteristic of the Monarch emulsion, and from it curve 2 was obtained by reducing the density at each point according to Fig. 5*a*. Although the reducing action is such as to take away a greater proportion of the low densities, it will be seen that curve 2 shows an inferior gradient at the end-point to curve 1, since a decrease in slope is produced between the points P and Q.

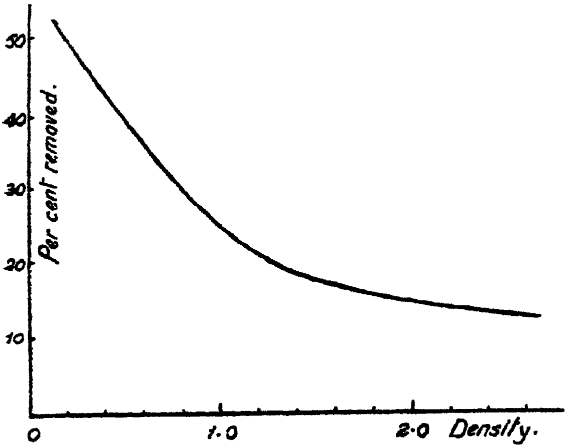

Fig. 5A.

This decrease in slope is partly counteracted by the fact that the line on the reduced plate is being compared against a less dense background of fog, but in practice the writer found no ultimate improvement.

Intensification processes were found to increase the density gradient along the lines, but the fogging produced made the end-points very indistinct. The method of making positive prints on process plates was also tried, in an effort to utilise both the speed of the Monarch emulsion, and the contrast of the Process emulsion, but the end-points were found to be no more distinct, due, partly, to the "graininess" produced. Trial was made of giving the plates a preliminary development, followed by reduction, so as to bring out and remove the "latent" fog incidental to manufacture.

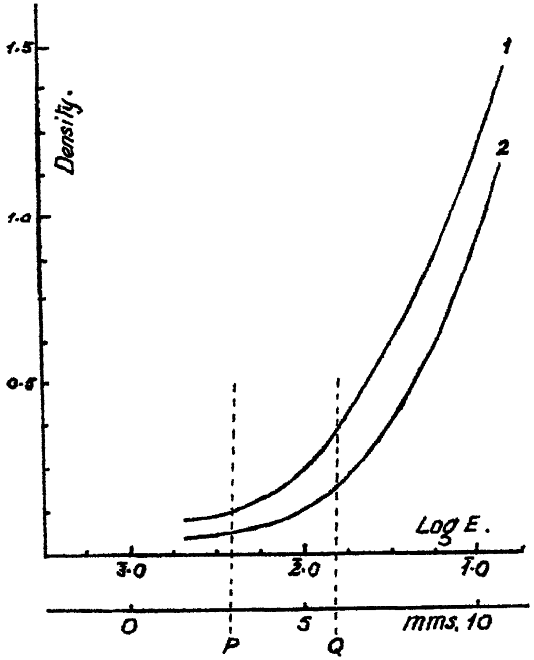

Fig. 5B.

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[5] *Handbuch d. wiss. angew. Phot.*, 1932, 5, 347.

When the final development, after exposure, was made, however, the total time spent in the hydroquinone was too long, and bad chemical fogging was produced.

The washing process, after fixation, was given considerable attention, in order to minimise the dirt and dust accumulating on the adhesive surface of the film, and ultimately a system was devised whereby the plates were given a 5-minute wash to remove most of the hypo, and placed in a cell, where they were measured under water. This, together with the microscope method of measurement, has already been described by Martin, Burke and Knowles (*loc. cit.*). Using this system it was found possible to measure the difference in length of two lines on the fast plates used with an accuracy of 0·2 mm., each line being measured twice.

The Internal Standard and Homologous Pairs.

Even with the most carefully controlled electrical circuits, a certain amount of fluctuation of the spark discharge is inevitable, so that it is necessary to employ the Internal Standard method of Gerlach and Scweitzer,[6] in order to obtain reproducible results, the ratio of two intensities being compared by measuring the difference between the lengths of two neighbouring lines.[1] One of the two lines is chosen from the spectrum of the element being estimated, while the other is a nearby line of another element called the "Internal Standard," which is present in fixed concentration.

Heretofore it has been considered necessary to select only lines which conformed to the condition of being "homologous pairs," that is whose intensities remained in fixed ratio with widely changing electrical conditions, and rigorous preliminary tests were conducted to ensure this, the choice of lines being thereby restricted. In the present work, however, the very weak emission from the spark made it necessary to confine the choice, as regards the lines of the element being estimated, to the *raies ultimes* of de Gramont, and since the range of available lines was still further restricted by the necessity of using only the ultra-violet region, and by the disturbing effects of background and insufficient dispersion, the idea of ensuring "homology" had to be abandoned.

To obtain the maximum sensitivity of the method, the writer found it necessary to select the most suitable *raie ultime* of the element to be estimated, and compare its length with that of the nearest line of the Internal Standard element. While this procedure might be expected to provide sufficient protection against slight changes in the illumination of the spectrograph, or in the properties of the photographic plate, it would seem, from the work of Gerlach and Schweitzer, that it must fail to produce the requisite constancy of intensity ratios under varying electrical conditions. It was found, however, that all the line pairs chosen behaved as homologous pairs with regard to the variations in conditions encountered in the present work. It would thus appear that if reasonable care is taken to prevent wide fluctuations, by, for example, keeping a constant spark gap width, the question of ensuring "homology" need not be considered.

Recirculation of Solution.

The only notable changes which might be expected to occur in the solution as a result of its passage through the spark gap are a slight rise in temperature and a gradual accumulation of gold ions due to electrolytic attack on the gold wire electrode. In practice the rise in temperature of 5° C. was counteracted by the use of an ice and water bath (see Fig. 1), and a set of measurements on a gold line in the spectrograms showed that the accumulation of gold was sufficiently slow to be neglected for practical purposes.

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[6] Gerlach and Schweitzer, *Die chemische Emissionsspectralanalyse*, of which Messrs. Adam Hilger have published a translation; "Foundations and Methods of Chemical Analysis by the Emission Spectrum," 1929.

Sufficient conductivity of the solution was obtained by the addition of 5 c.c. of concentrated hydrochloric acid to each 100 c.c. of sparking solution, as this has been found by the writer and by previous workers to be the best method. The evaporation from the slightly heated spray in the apparatus caused slight concentration of the acid, but investigation showed that the increase in strength was small enough to be easily negligible, since it will be shown that quite large increases in acid strength are permissible. The slight decrease in volume of the solution caused an increase in concentration of both the metallic ions whose intensities of emission were being compared, the ratio of the concentrations remaining unaltered.

It would thus appear that the solution, after being passed through the spark gap and cooled again, is unchanged for practical purposes, and may be used over and over again. Experiments to verify this were made, in which (*a*) a solution containing 0·1 per cent. of iron and 0·1 per cent. of chromium was recirculated 12 times, exposures being made for each recirculation, while the lines $Cr_{2762\cdot5}$ and $Fe_{2753\cdot7}$ were measured, and (*b*) a solution containing 1·0 per cent. nickel and 0·5 per cent. iron was recirculated 70 times, the lines $Ni_{2416\cdot1}$ and $Fe_{2409\cdot9}$ being measured.

In the first case the difference in length of the iron and chromium lines was found to be constant, within the limits of experimental error, while in the second case the difference in length between the nickel and iron lines remained constant up to about 40 recirculations. These results show that a considerable increase in the sensitivity of the method can be achieved by the recirculation of the solution.

In the case of the nickel and iron lines, both the lines decreased progressively in length, until after 40 recirculations they became too short to measure. All the lines in the spectrum below about 2480 A.U. were similarly affected, while lines of longer wavelength appeared to suffer little or no diminution of intensity. The effect appeared to be due to absorption by some vapour surrounding the spark, possibly chlorine, hydrogen peroxide, or hypochlorous acid,[7] formed by the continued electrolysis of the hydrochloric acid electrolyte. With the *raies ultimes* involved in this research, only nickel was effected by the above phenomenon, and using a pair of lines which were close together, their intensities remained in constant ratio, so that the measurements could still be relied upon while both lines remained visible on the plate.

Interference of one Metal with another.

Twyman and Hitchen[2] have published curves showing that the presence of a third kind of ion in solution, in addition to the two being compared, generally has a marked effect on the intensity ratios of the latter. Such a conclusion, if verified, would greatly complicate the experimental procedure in those cases where the solution contained several ions, as in the case of corrosion liquors. The earlier work on the log sector was, however, subject to certain sources of inaccuracy, such as errors in the figuring of the sector periphery, and the above workers' conclusion that in some cases 2·5 per cent. of a disturbing element had a bigger effect than 5 per cent. led the present writer to investigate the matter more closely.

Exposures were made on solutions containing 0·01 per cent. chromium, and 0·1 per cent. iron, with varying amounts of manganese up to 0·1 per cent. as the third or disturbing element. The series was continued with 0·1 per cent. chromium, 0·1 per cent. iron, and manganese up to 1·5 per cent. No effect on the difference in length of the lines $Cr_{2762 \cdot 5}$ and $Fe_{2755 \cdot 7}$ was found within the limits of experimental error.

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[7] Fergusson, Slotin and Style, *Trans. Faraday Soc.*, 1936, **32**, 956.

A further series of experiments was carried out with solutions containing 0·1 per cent. iron, 0·01 per cent. manganese, and varying amounts of nickel up to 5 per cent. The lines $Fe_{2599 \cdot 4}$ and $Mn_{2593 \cdot 7}$ were measured, and the difference in length was again found to be constant within the limits of experimental error. It may thus be said that, so far as the metals involved in the present research are concerned, the intensity ratios of a line pair are unaffected by the presence of other elements in the solution, for the experimental conditions and within the range of concentrations specified.

The examples given above are, however, insufficient to justify a general conclusion, and more data are necessary before a comprehensive decision can be taken on the existing conflicting evidence.

Calibration Curves.

It is always necessary to plot curves showing the manner in which the difference in line-lengths varies with the concentration of solutions of known composition, and the resulting curve can then be used to give results from exposures under identical conditions on unknown solutions. In both cases the solutions contain an Internal Standard element in fixed concentration, and also the element to be estimated. In the estimations of the elements in the corrosion solutions, it was assumed that the other metals present in the solution had no interfering effect, and hence no effort was made in the calibration experiments to reproduce the exact composition of the corrosion liquors by adding the appropriate amounts of other metals. Hence the solutions for the calibration exposures contained only the Internal Standard element and the element to be estimated, with the addition, as usual, of 5 per cent. hydrochloric acid.

In order to avoid complicating the composition of the solutions still further, and in order to prevent the addition of still more lines to an already complex set of spectra, it was decided to use one of the four metals, iron, chromium, nickel and manganese, normally present in the corrosion solutions, as Internal Standard by making its concentration equal to the standard fixed value. The optimum concentration of Internal Standard depends on several factors. Too high a concentration is to be avoided since the spectrum becomes unduly complicated, and background is increased, while impurities in the chemicals used to provide the Internal Standard metal may become serious with high concentrations. On the other hand it is advisable to make the concentration sufficiently high to enable the amount of metal produced by the corrosion to be neglected in comparison, a fixed excess being added before each estimation.

Iron was chosen as the Internal Standard for estimating chromium, nickel, and manganese since its spectrum offered a sufficient choice of lines. A concentration of 0·1 per cent. was found to be most suitable, having regard for the above considerations, but later it was found that the higher value of 0·5 per cent. had to be used in the estimations of nickel and manganese in order to get enough of the latter metals in solution for analysis, since the concentration of iron from the corrosion increased at the same time. The calibration curves thus obtained are shown in Fig. 6. Manganese was chosen as the Internal Standard for the estimation of iron, and a concentration of 0·01 per cent. was employed, since the line used was very intense, and also because the concentration of manganese from the corrosion is always low. The resulting calibration curve is shown in Fig. 6. Each of the points in Fig. 6 is the average of three exposures to allow for local irregularities in the emulsion.

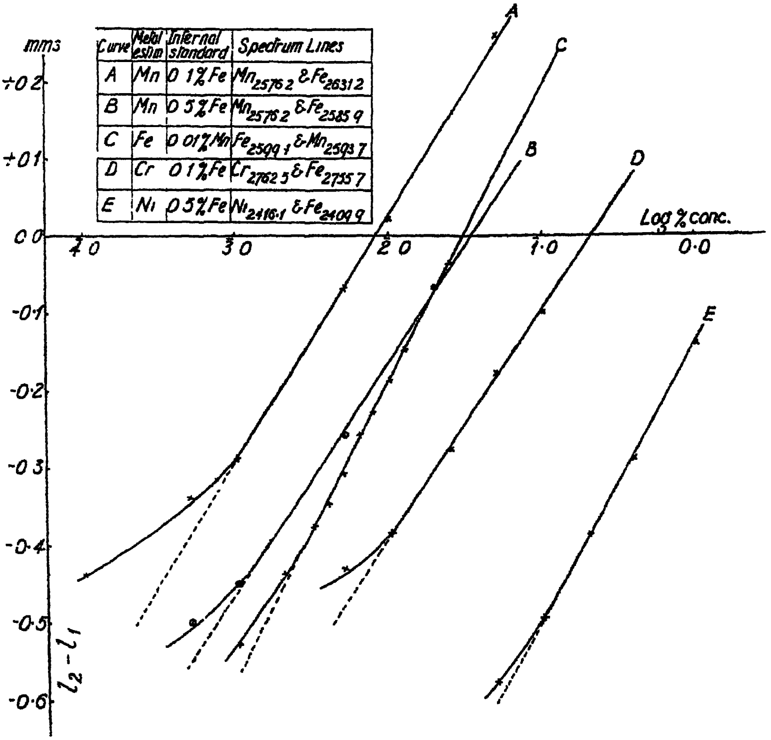
It will be seen that, except for a slight bend at the foot of each curve, the points all lie on a straight line when the difference in line-length is plotted against the logarithm of the concentration. This linearity bears out the validity of the equation :

$$\frac{l_B}{l_A} = kc^n \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

and the numerical relation :

$$0{\cdot}2p\ (l_2 - l_1) = m \log_{10}(kc^n). \quad . \quad . \quad . \quad \text{(ii)}$$

These equations were originally derived by Twyman and Simeon[1] with the omission of the constants m and n. The necessity for including the index n was pointed out by Martin, Burke and Knowles[2] on account of measurements to be described in the present paper. The magnification m of the spectrograph is now included in equation (ii) above, so that l_2 and l_1 are now the lengths of the lines as measured on the plate, instead of on the slit.



Curve	Metal estim	Internal standard	Spectrum Lines
A	Mn	0 1% Fe	$Mn_{2576\,2}$ & $Fe_{2631\,2}$
B	Mn	0 5% Fe	$Mn_{2576\,2}$ & $Fe_{2585\,9}$
C	Fe	0 01% Mn	$Fe_{2599\,4}$ & $Mn_{2593\,7}$
D	Cr	0 1% Fe	$Cr_{2762\,5}$ & $Fe_{2755\,7}$
E	Ni	0 5% Fe	$Ni_{2416{\cdot}1}$ & $Fe_{2409\,9}$

FIG. 6.

Deviations from Linearity. Effect of Intermittency and Background.

At the foot of each of the curves shown in Fig. 6, there is a deviation from the linearity exhibited by the remainder of the points, and the effect appears to be a fairly general result of making measurements on a very short line. A somewhat similar effect was found by Twyman and Harvey[3] in their experiments on the relation between line-length and intensity. They suggested it might be due to variations with intensity of the straight part of the emulsion curve or to deviations from the true Schwarzschild relation, and concluded that the effect was operative only in the case of slow plates.

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[3] Twyman and Harvey, *Trans. Opt. Soc.*, 1931-32, 33, 1.

The present work with fast plates shows that it is not dependent on the emulsion speed, and there is no evidence to show that the Schwarzschild relation or the position of the emulsion curve alter for lesser intensities. The effect takes the form that short lines exhibit a length greater than that consistent with linearity, and the writer has observed that the deviation is greatest in cases where the background intensity is most pronounced, and only becomes noticeable when the line-length shortens to a value comparable with the length of the background lines. The cause would thus appear to be the additive effect of background, the constant intensity of which slows up the rate of shortening as the line intensity falls off to low values. Thus curve E for the nickel line 2416·1 A.U., which is in a region of low background intensity, showed little deviation even for the shortest line-lengths, while the effect was more pronounced with $Mn_{2576\cdot2}$ and $Cr_{2762\cdot5}$, as shown by curves A and D.

From the practical point of view the bend at the foot of the calibration curves need cause little difficulty so long as the background intensity is kept reasonably constant by sufficient control over the conditions of excitation, so that the position of the curve remains fixed during the calibrations and the estimations. Since, however, a given error in measuring the lines corresponds to a greater error in estimating the concentration of the solution on this less steep portion of the calibration curve, the accuracy of the method is diminished. Moreover the Internal Standard idea is not fully effective in this region, since fluctuations in the conditions do not affect the total intensity of the shorter line to the same extent as a long one, because of the constant background component included in the former.

In any accurate application of the log sector the question of intermittent exposure cannot be neglected. The longer lines have a greater pause/light ratio, and so tend to lose a greater portion of their photographic effect. A further intermittency effect occurs through the oscillations of the spark. It is difficult to ascertain the extent to which these influences affect the photographic density, but the linearity of the calibration curves does not appear to be affected.

The effect of intermittent illumination might, however, make itself apparent by altering the slopes of the calibration curves without impairing their linearity. It is probable that the intermittency of the sector causes a slight diminution in the effect of the larger intensities, so as to make the effective value of the Schwarzschild Constant nearer to unity than it would be with continuous exposures. Thus Twyman and Harvey[8] and Baly, Morton and Riding,[9] have measured the Schwarzschild Constant for sector work, and find it to be either unity or just less than unity. The abnormal slopes mentioned below could, however, hardly be accounted for in this manner, since the effective value of the constant would have to be raised well above unity to explain the whole effect.

The Slopes of the Calibration Curves. The constants *m* and *n*.

From equation (ii) it is seen that the slope of a curve of $(l_2 - l_1)$ plotted against $\log_{10} c$ should be equal to $5mn/p$, and since the effective value of p, the Schwarzschild Constant, has been shown to be almost unity for sector work, and the value of m is easily measured, the measurement of the slopes of the calibration curves offers a means of determining the value of n.

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[9] Baly, Morton and Riding, *Proc. Roy. Soc.*, *A*, 1926, 113, 709.

Previous workers have assumed that the intensity of emission was proportional to the concentration, and therefore omitted the index n altogether. The linearity of the results connecting line lengths with concentration was supposed to support this view, but Martin, Burke and Knowles[3] showed that the linearity merely proved equation (i). Twyman and Hitchen's results for zinc, cobalt, nickel and bismuth, plotted logarithmically, gave slopes between 2·7 and 3·1, values so much less than 5 that it is improbable that the divergence was due to the magnification m alone.

The magnification of the E. 3 quartz spectrograph over the range of wavelengths involved in this research was measured by making a series of measurements of the lengths of the lines produced on the plate at different parts of the spectrum by a slit length of exactly 1 centimetre, cut off by a V-diaphragm, the measurements being made accurately by a travelling microscope.

TABLE I.

Metal.	Wavelength. A.U.	Slope.	Magnification.	Value of n.
Chromium .	2762·5	2·9	0·87	0·63
Iron . .	2599·4	3·8	0·87	0·83
Manganese	2576·2	3·1	0·85	0·69
Nickel . .	2416·1	3·6	0·85	0·80

The results, together with the slopes of the calibration curves, are shown in Table I. The value of p was taken as 0·95. The value of n thus calculated is seen to fall well below unity, and it cannot thus be omitted from equation (i). The theoretical significance of the index is obscure and it is conceivably due to absorption by the vapour round the spark, rather than to a lack of proportionality between the emission intensity and the concentration. It is unlikely to be due to an intermittency effect, as already stated, and the latter would give no explanation of the variation in slope from one line to another in the same part of the spectrum. There does not appear to be any relationship between the value of n and the wavelength.

The Accuracy of the Method.

It has been stated that the microscope and water cell method of measurement enables the difference in length of two lines to be measured on fast plates with an accuracy of 0·2 mm. The error on an average of three exposures is naturally less, and it will be seen that in Fig. 6 practically all the points lie within 0·1 mm. of the curve. From equation (ii) we see that—

$$0{\cdot}2p\,(l_2 - l_1) = 0{\cdot}434\,mn \log_e c + const.$$

whence

$$\frac{dc}{c} = \frac{0{\cdot}2p}{0{\cdot}434} \times \frac{1}{mn} \times d(l_2 - l_1).$$

Taking a value of 0·95 for the Schwarzschild Constant p, the percentage error in the concentration c produced by an error of 0·1 mm. in line measurement becomes

$$\frac{dc}{c} \times 100 = \frac{4 \cdot 4}{mn} \quad . \quad . \quad . \quad . \quad \text{(iii)}$$

Since the value of mn is about 0·6 in practice, the probable percentage error of the method is about 7-8 per cent., provided the value of the

Schwarzschild Constant does not vary much between the calibrations and the estimations. When it is necessary to use the lowest, non-linear, portion of the calibration curve, it is impossible to attain the above degree of accuracy, however, for various reasons. As already mentioned, the smaller rate of change of line-length with concentration in this region diminishes the accuracy, while the protection afforded by the Internal Standard against electrical fluctuations may be less. It was found, moreover, that the end-points of short lines were less sharp, so that their measurement was liable to greater inaccuracies. The cause of this variation in the endings is obscure. Errors of up to 15 per cent. may thus occur when estimations on very weak intensities have to be made, using the lowest part of the curve.

The Sensitivity of the Method.

From the lowest concentrations in Fig. 6 it will be seen that the smallest weights of metal required for an analysis are the following, since 20 c.c. of solution are necessary :

Chromium . .	0·001 gm
Manganese . .	0·00004 ,,
Nickel . . .	0·01 ,,
Iron . . .	0·0002 ,,

The sensitivity of the nickel estimation is low on account of the absence of intense nickel lines in the ultra-violet above 2500 A.U.

Changes in the Value of the Plate Constants.

Clearly slight changes in the value of the speed or contrast factors will not affect the difference in length of two lines, but changes in the Schwarzschild Constant produce errors in accordance with equation (ii). The effect of a change in value from 0·95 to 0·90 is shown graphically below, the two lines being the calibration curves for the two cases, and it will be noted that they cross at a zero value for the difference in line-length, since the L.H.S. of equation (ii) must then be zero in any case.

The slope of the calibration curve alters in inverse proportion to p, and the error resulting from using an old calibration curve with new plates, whose value of p is different, is greatest for the more negative values of the difference in line-lengths, that is for the shortest lines. At the foot of the curve, where the slope is less, such errors are especially serious. From the measurements which have been made on the Schwarzschild Constant for sector work, it seems improbable that the value of p varies by more than 2 or 3 per cent. from one batch of a given type of plate to another. Hence, since the greatest difference in line-length used in practice is 5 mm., the largest error which could be caused by a change in the Schwarzschild Constant is probably 0·1-0·15 mm.

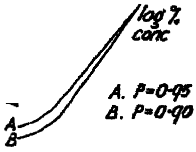

Fig. 7.

Effect of Different Acid Electrolytes.

The calibration curves were all made with a standard 5 per cent. hydrochloric acid electrolyte, but in actual corrosion analysis it is often impossible to reproduce these standard conditions conveniently, so that it is important to know the degree of latitude which is permissible in applying the results of calibration in one electrolyte to estimations in another. A number of comparative experiments were carried out, and it was found that, within the experimental error of the method, the results were identical up to

50 c.c. conc. HCl or 33 c.c. conc. HNO_3 or 50 gm. conc. H_2SO_4 per 100 c.c. sparking solution.

Marked absorption effects occur, however, below about 2450 A.U. with strong solutions of HCl or HNO_3, but not with H_2SO_4, a slight increase in length of the lines being observed in the latter case. In certain cases the nickel lines were thus rendered too short to measure, but the difference in line-lengths appeared to be unaltered. The effect may be due to absorption by hydrochloric acid vapour or chlorine round the spark.

The Application to Corrosion Problems.

The usual procedure in investigating the progress of corrosion reactions is to determine the loss of weight of the metal specimen, but a number of indications of the rate of attack have been employed in certain cases, such as electrode potential, electrical resistance, tensile strength, hydrogen evolution or oxygen absorption. The loss of weight of a piece of metal immersed in a solution sometimes does not yield a reliable estimate of the amount of chemical attack, since the opposing factors of oxide deposition and dissolution of metal may both operate simultaneously, although sometimes it is possible to remove the oxide chemically without causing further attack on the metal. A convenient method of analysing the solution in which the metal has corroded offers certain advantages, and it is felt that the log sector method might prove of utility on account of its speed and simplicity.

The metal specimens used for this investigation were samples of stainless steel, which Dr. Hatfield of the Brown-Firth Research Laboratories very kindly supplied, and of which Table II. shows a typical analysis :—

TABLE II.

	Steel A (Saitie).	Steel B (Staybrite).
	Per Cent.	Per Cent.
Iron .	84·3	73·4
Chromium	14·1	18·1
Nickel .	0·79	7·62
Manganese	0·35	0·28
Carbon .	0·014	0·028

Each steel also contained small quantities of silicon, sulphur and phosphorus. After suitable abrasion and degreasing, weighed pieces of the steel were supported on glass triangles in beakers containing the corroding liquid, the metal being completely immersed beneath the surface. The beakers were supported in an electrically heated thermostat kept at 25° C., and the contents of the beakers were kept stirred continuously.

Samples of the solution could be taken at intervals, or the whole of the solution could be replaced by fresh corroding liquid, without interfering with the progress of the reaction, and as many as possible of the metals, iron, chromium, nickel, and manganese were then estimated after adding the appropriate amounts of acid or Internal Standard when required. The best method of arranging the estimations was found to be as follows. The solution from the corrosion was divided into two portions, and the smaller portion was somewhat diluted and sparked for the estimation of iron, after adding 0·01 per cent. manganese Internal Standard. From the result of the iron estimation, the amount of iron necessary to raise the total concentration to 0·1 per cent. was calculated, and chromium was estimated in the same solution against 0·1 per cent. iron as Internal Standard.

The larger portion of the corrosion solution was then concentrated to the volume calculated to give 0·5 per cent. iron, and the estimations of nickel and manganese were carried out simultaneously.

The above procedure requires, in some cases, a small correction on account of the manganese already in the solution before adding a further 0·01 per cent. as Internal Standard. It was found that over the range of attack examined, the metals dissolved in the same proportions as they were present in the steel, and since the ratio of Mn to Fe in the steel was known to be about 1 : 250, the concentration of manganese in the solution could be calculated approximately from a knowledge of the iron concentration. The manganese concentration was thus usually found to be about 0·0002 per cent. higher than the standard value, and a small correction on the iron estimation was made accordingly.

It will be noticed that the above procedure makes the estimations of chromium, nickel and manganese dependent on that of iron, but since the iron estimation is generally accurate to about 5 per cent. on account of the fact that there is usually sufficient metal present to enable the straight part of the calibration curve to be used, the errors thus caused are generally small. Where strong acids were concerned, the solution for the estimation of nickel and manganese had to be evaporated to dryness and made up with 5 per cent. HCl, in order to avoid the absorption effect found to interfere with the nickel estimation, as already described.

Corrosion 1.

Six approximately similar cylindrical specimens of steel B of total surface area 102 sq. cm. were supported with their axes vertical immersed in 100 c.c. of 5 per cent. HCl, which was replaced every 24 hours. Iron, chromium and nickel were estimated in the solution, but manganese was not estimated.

The results are shown in Table III. in grams, and the weights of nickel shown are those accumulated over periods of two and three days respectively, in order to obtain enough for analysis. The total weight of metal found in solution by adding together the results of the above analyses, namely 0·494 gm. was found to agree within the limits of experimental error with the loss of weight of the steel cylinders, namely 0·465 gm.

TABLE III.

Sample.	Time.	Time.	Chromium.	Nickel.
1	1 day.	0·089	0·019	—
2	2 ,,	0·080	0·017	0·021
3	3 ,,	0·062	0·011	—
4	4 ,,	0·078	0·017	—
5	5 ,,	0·062	0·014	0·024

Corrosion 2.

Six cylinders of steel B of total area 102 sq. cm. were immersed in 500 c.c. of 1 per cent. HCl. After the first 2 days, the reaction became very slow, and only iron could be estimated, but an analysis of chromium was also made in the first solution sample (Table IV.).

The weight of metal accounted for by the estimations of iron and chromium was 0·051 gm., while the loss of weight of the cylinders was 0·056 gm., part of the difference being the unanalysed nickel. It will be noticed that a remarkable change took place in the velocity of the corrosion after about 2 days, or possibly earlier, the rate of attack slowing up in the ratio 1 : 1000, possibly due to the formation of a protective film. It may be remarked that this phenomenon would be more likely to escape observation with the usual weight loss method of investigation, since there are objections to removing the piece of steel from solution, for drying and weighing on account of the likelihood of a change in the surface condition being thereby produced. The method of solution analysis thus offers advantages by furnishing data at several stages in the reaction.

TABLE IV.

Sample.	Time.	Iron.	Chromium.
1	2 days.	0·042 gm.	0·0076 gm.
2	22 ,,	0·0004 ,,	—
3	42 ,,	0·0012 ,,	—

Corrosion 3.

Two flat pieces of steel B, of total surface area 23 sq. cm., were immersed in 10 c.c. of 20 per cent. (by weight) sulphuric acid, the acid being changed for analysis every 12 hours. The results are shown in Table V. in grams.

TABLE V

Sample.	Time.	Iron.	Chromium.	Nickel.	Manganese.
1	12 hours.	0·125	0·034	—	—
2	24 ,,	0·014	0·028	0·028	0·0008
3	36 ,,	0·110	0·034	—	—
4	48 ,,	0·141	0·034	0·030	0·0008

The sum of the weights of metal found in solution is 0·671 gm., while the weight loss of the steel was 0·604 gm.

Corrosion 4.

A flat piece of steel A, of total surface area 40 sq. cm., was immersed in 250 c.c. tap water (iron-free within the limits of the log sector method) for 40 weeks, causing slight pitting of the surface. On removing the steel, any loose adhering deposit was washed off with a jet of water, and added to the solution for analysis.

On analysis 0·0006 gm. of iron was found in the solution, but when the steel was weighed it was found to have gained in weight by 0·0027 gm., owing, presumably, to the deposition of oxide on the surface. Removal of the oxide by, for example, nitric acid of the appropriate strength, would enable a fairly reliable estimate of the degree of attack to be obtained from the weight loss, provided the amount of metal dissolved away at the same time by the acid could be allowed for accurately, or neglected, but the analysis of the solution, together with the gain in weight of the steel, give useful information from another angle.

Discussion of Results.

The above corrosions are typical examples of the experiments made to apply the log sector method to such problems. It will be seen that almost all the results in corrosions 1, 2 and 3 show that, within the limits of experimental error, the metals dissolved in the same proportions as they existed in the solid steel. Thus no preferential attack could be discovered with the sensitivity of analysis available, the effect, if any, being hidden by general solution.

The apparently wide range of conditions and composition of the solution in which the log sector method is capable of making analyses with simplicity and rapidity, suggests that it might have a sphere of utility in such cases as the examination of foodstuffs for contamination from metallic containers, or the investigation of complex industrial liquors for contamination by the plant with which they come into contact.

The author is greatly indebted to Assistant Professor L. C. Martin, D.Sc., for valuable advice during the course of the work, and to Messrs. Adam Hilger, Ltd., for the loan of part of the apparatus used.

THE PEPTISATION OF AQUEOUS SOAP SOLUTIONS.

By A. S. C. Lawrence.

Received 2nd November, 1936.

Various substances have been added to soaps for commercial purposes: alcohol and cane sugar[1] to make it transparent: phenol and cresols as disinfectants: glycerin is recommended for soap solutions for blowing bubbles.[2] But their action has been overlooked or incorrectly explained. The improvement by glycerin has been attributed to its increasing the viscosity thereby reducing local variations in the soap films. Apart from the fact, already pointed out by the writer,[3] that this explanation is fallacious, glycerin reduces the viscosity at all but very small concentrations of soap. Without glycerin, many soap solutions have "anomalous viscosity" (possibly only below their Krafft points) and therefore very large apparent viscosity when the deforming force is small. On addition of glycerin from 10 per cent. upwards, the solutions become Newtonian liquids which give very much better lasting films than the solutions containing no glycerin and possessing a small rigidity[4] Cane sugar has a similar effect.

It has been known for a long time that phenol and cresol are very much more soluble in soap solutions than in water but no attention seems to have been given to the fact that the increase is mutual, except in a paper by Lester Smith[5] who notes this fact and also points out that it cannot be explained by an adsorption mechanism.

Measurements have been made of the amount of cresol held as gel by 1 gm. of various soaps; also the minimum amount of soap required to hold 50 per cent. of cresol in solution.[6] Angelescu and Popescu have gone farther in elucidating the action of cresol by recognising that they were dealing with a three component system.[7] They measured the viscosity of oleate-cresol-water system and found that gelation is only the first stage of an action which, with larger amounts of cresol, is clearly seen to be a peptisation. The viscosity rises sharply to a maximum and then, with more cresol, falls again. The action of some peptisers on soap films has been described.[8]

It is now found that numerous alcohols, phenols and amines exert a similar action, *i.e.*, when a small amount is added to a soap/water mixture, the viscosity rises sharply, a stiff gel often being formed. Then further addition reduces it, usually below the original value. The amount of peptiser required to produce these changes depends upon its solubility in water since there is a distribution between soap and water.

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[1] C. Steipel (*Fette, Öele und Wachse*, Leipzig, 1911, p. 192) remarks that sugar tends to keep soap transparent . . . "how the sugars accomplish this is not yet settled."

[2] Dewar, *Roy. Inst. Proc.*, 1923, **24**, (1) 199. Collected Papers 2, 1336.

[3] A. S. C. Lawrence, *J. Physic. Chem.*, 1930, **34**, 263.

[4] A. S. C. Lawrence, *P.R.S.*, 1935, 59.

[5] *J. Physic. Chem.*, 1932, **36**, 1401.

[6] Jenčič, *Koll. Z.*, 1930, **53**, 10; 1927, **42**, 168.

[7] *Koll. Z.*, 1930, **51**, 256.

[8] W. J. Green, *Nature*, 1933, 872.

Much larger amounts of the easily soluble peptisers are therefore required since they tend to remain in the water without interaction with the soap.

Peptisation was observed qualitatively with the following substances: a $N/10$ solution of sodium stearate was prepared and, after taking off a blank sample which was left to cool, small amounts of the trial substances were added. The mixing was usually carried out with warm soap solution to avoid the early gel stage. The blank set to the usual lump of curd. Where peptisation occurred, a clear solution was obtained or, in the case of solid peptisers, a solid with lower setting point than the blank and differing in structure from it. The normal saturated alcohols up to C_{12} form liquid systems at room temperature. So do phenol, cresol, cyclohexanol, benzyl alcohol, aniline and phenylhydrazine in small concentration. Glycerin and glycol are efficient in larger amounts and ethyl alcohol moderately so. Thymol, the naphthols, benzidine and camphor all peptise at higher temperature but deposit solid on cooling.

The more concentrated soap solutions, when peptised, become miscible with excess of the peptiser: *e.g.*, with amyl alcohol in all proportions; and with hydrocarbons.[9] Addition of caustic soda does not salt out the soap from the peptised solution but addition of acid or of a metal salt gives a precipitate. Potassium, ammonium and lithium soaps are also peptised by the same substances but they have no action on the insoluble metallic soaps.

Cetyl sodium sulphate is peptised by the same substances but the effects are very much less marked. Aniline cetyl sulphate solutions form a gel on cooling from which crystals separate.[10] If excess of aniline is added, the gel stage is cut out.

Quantitative Results.

With soluble substances, such as ethyl alcohol and glycerin, a saturation end-point cannot be obtained directly but the point at which the viscosity is reduced to the same order as that of water serves as a satisfactory end-point. To reach this required very much larger amounts of the soluble substances than of the slightly soluble ones. In Fig. 2 a single result for tertiary amyl alcohol shows that about three times as much of the tertiary alcohol as of the primary is held by the soap at saturation. The solubility of the tertiary alcohol is also about three times that of the primary in water. It is clear that there must be a distribution of the added peptiser between soap and water and in the case of peptisers miscible with water it is impossible to find directly how the substances are distributed. The case of the amyl alcohols is therefore particularly interesting since it shows that solubility in soap and in water are parallel whereas, if adsorption on to the hydrocarbon tail of the soap molecule occurred, the solubilities would move in opposite directions.

Fig. 1 shows the results for amyl alcohol and three soaps of the saturated series—C_8, C_{12} and C_{18}. A known weight of soap was dissolved in water. To part of this solution the alcohol was added until saturated. The end-point is easily determined since as soon as excess of alcohol is present it remains at the surface of the solution and " kills " the foam. With aniline, the saturation point is less easy to determine since the excess sinks to the bottom and while the solution is in motion is not easily distinguished from air bubbles. In these cases excess of aniline was added. This, on standing separated and its volume was determined and subtracted from the total added. Further samples of the soap solution were then diluted to appropriate dilutions and the amounts of peptiser required for saturation determined in the same way.

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[9] One such system of hydrocarbon in soap solution peptised by amyl alcohol, apparently homogeneous, on re-examination after three weeks was found to have segregated into two clear layers. It is possible that we are here dealing with an emulsion in which the interfacial tension is abnormally small—too small for retention of the spherical form of the disperse phase when stirred. The large excess of soap would be expected to cause instability. Pickering (*J.C.S.*, 1917, 86) has described the taking up by concentrated soap/water systems of large amounts of oil to form stable mixtures. The stability of his mixtures in the presence of very large excess of soap would be explained by hindrance to segregation caused by the plastic state of the system.

[10] Private communication from Dr. G. S. Hartley.

The results in Fig. 1 show the total solubilities of peptiser in water and soap. The amount added is plotted against the volume of water in which the given weight of soap is dissolved. The amount held by the soap, in the cases of laurate and stearate is the intercept on the axis corresponding to zero water. The slope represents the solubility of the amyl alcohol in water. This agrees with the published data. Sodium caprylate is obviously quite different from the higher soaps. It was selected because McBain's results show it to be half crystalloidally and half colloidally dissolved at 90° C. It is clear from Fig. 1 that as its solutions become more dilute, less alcohol is taken up.

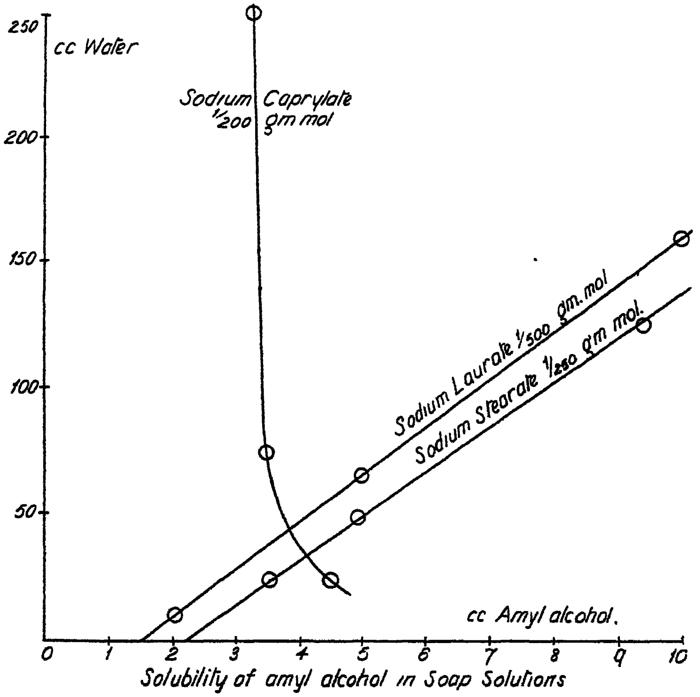

FIG. 1.

The meaning of these results is more clearly shown in Fig. 2 in which the amount of amyl alcohol and aniline dissolved in the water is subtracted from the total and the amount held by the soap plotted against its concentration. The amounts are calculated to give the number of molecules of peptiser per molecule of soap. It is clear that less alcohol is taken up as the hydrocarbon chain of the soap molecule increases. This is another point against an adsorption mechanism. Sodium valerate solutions are not affected by amyl alcohol. Sodium acetate salts it out from aqueous solution. The less soluble hexyl and heptyl alcohols reach saturation at a ratio of about 4 molecules per molecule of soap. From these solutions a considerable amount of the soap separates at room temperature. Quite small amounts of oleyl and cetyl alcohols are taken up: less than 1 molecule per molecule of soap.

Experiments were carried out with sodium stearate and aniline to find the effect of partial peptisation. Aniline, in various amounts less than the saturation value, was added to hot $M/3$ solutions of sodium stearate and the setting point observed.[11] Fig. 3 shows the results. It shows that most of the peptisation is complete before saturation is reached but there is still no evidence of any simple stoichiometric relation.

The temperature coefficient of absorption of peptiser was examined in the case of $M/6$ sodium stearate and aniline. Sufficient aniline was added to saturate the soap at 100°. The excess was measured and the increase of free aniline observed as the temperature fell. At 100° the density difference is just sufficient for the excess aniline to collect at the surface but as soon as the mixture cools the aniline becomes denser faster than the soap solution with the result that no observations can be obtained until it has cooled to 45° by which time the aniline forms a coherent layer at the bottom. Between 45° and 100° it forms spheres which wander about suspended in the solution. Fig. 4 shows the results. Curve 1 shows the total amount of aniline taken up. Curve 2 is the solubility of aniline in water, and curve 3 is the difference between the two: that is, the amount of aniline held by the soap. The temperature coefficient of this is very small. There is no discontinuity in the cooling curve.

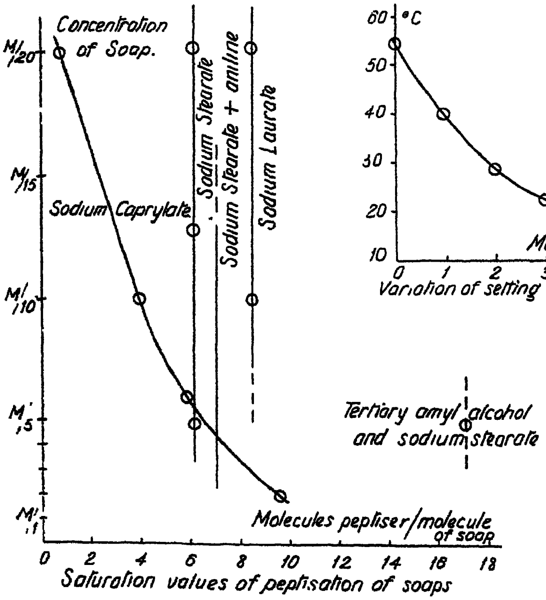

FIG. 2.

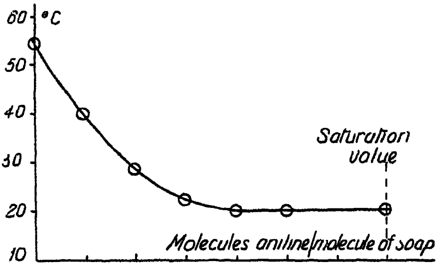

FIG. 3.

In a number of cases where the substance added was a solid (*e.g.*, camphor, the naphthols, naphthylamines, benzidine), peptisation occurred when the solutions were boiled but on cooling solid separated. It was usually impossible to separate the solid by filtration but in two cases this has been done and analysis showed that the complex formed in solution is broken down on solidification. A 10 per cent. solution of sodium stearate was peptised fully by amyl alcohol, cooled quickly to room temperature and poured into a measuring cylinder. Any excess of alcohol separates and the amount is measured. After some hours crystallisation occurs accompanied by elimination of amyl alcohol. The amount of alcohol was measured and the solid was then filtered off, dried and weighed. The two amounts were equivalent: that is, crystallisation involves breakdown of the complex existing in solution.

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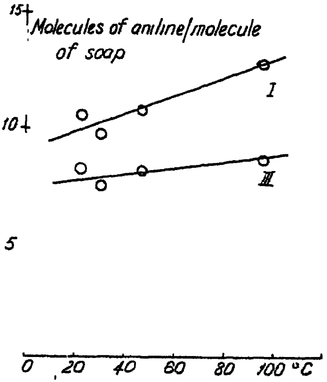
[11] Krafft (*Ber.*, 1895, **28**, 2566), observed that soap solutionss how a sharp break in their temperature/solubility curves and that, at this temperature, the solution solidifies as most of the soap separates out. Sodium soaps harden to "curd" at a temperature a little below the Krafft point and quite distinct from it (A. S. C. Lawrence, *Trans. Faraday Soc.*, 1935, 193). In the homologous series of the sodium soaps of the saturated fatty acids the "Krafft" point is parallel and close to the melting-point of the fatty acid present. In each soap it falls somewhat with increasing dilution but at any fixed concentration it is a quite definite characteristic of the system.

Schulman has obtained evidence of the existence of a complex of cholesterol and sodium cetyl sulphate in monolayers.[12] Alcoholic solutions of the two substances are mixed and poured into water, in which the complex remains stable. We found, however, that if the mixed alcoholic solutions are allowed to crystallise, the two substances are recovered quantitatively, the sodium cetyl sulphate coming out first while the cholesterol separates on cooling the mother-liquors in ice. No precipitate is formed on addition of silver nitrate to the aqueous solution of this complex of such strength that, without the cholesterol, the sodium cetyl-sulphate solution gives a copious precipitate of the silver salt. This soap also loses its marked hæmolytic activity when bound in the complex.



Temperature. Variation of amount of aniline taken up by Sodium stearate

FIG. 4.

Discussion.

The chief difficulty in explaining these observations is that the soap/water systems themselves are not fully understood. On cooling a hot solution of a soap, the following changes occur:—

(1) Hot solution; optically empty; soap partly molecularly dispersed, partly colloidally as small micelles—some 30 molecules per micelle. McBain's classical work was carried out in this region.

(2) On cooling, a point is reached where the solubility is suddenly largely reduced and the system becomes slightly opaque and very viscous. This is the state of soft soap.

(3) On further cooling, an abrupt transition occurs to the very opaque hard white curd. The temperature difference between 2 and 3 is small. Krafft did not distinguish between the two phenomena nor have subsequent writers.

Potassium soaps do not reach stage 3 at ordinary temperatures and remain as soft soaps. If however, they are salted out with sufficient KCl curd is formed. The long-chain sulphates and sulphonates do not pass through the soft soap stage but crystallise directly from stage 1 to stage 3. This presumably is because their temperature of transition to curd is above their Krafft points. Under certain unknown conditions sodium cetyl sulphate actually does pass through stage 2 forming a slightly opaque elastic liquid similar to the aniline cetyl sulphate already mentioned. From the elastic liquid, the normal crystals of stage 3 separate on standing.

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[12] Private communication from Dr. J. H. Schulman of this Laboratory.

It has already been suggested by the writer that the intermediate soft soap stage is due to formation of secondary micelles by aggregation of the primary micelles by association of their exterior — COONa groups.[13] The action of the peptiser is then easily explained as prevention of this association by dipole interaction between peptiser and these polar groups. When the temperature is lowered so far that the complex is no longer soluble, association to the curd phase follows with elimination of the peptiser. The only difference between the normal curd and that deposited from the peptised solutions is that the former grows from the long very thin micelles of the secondary stage and is therefore very bulky whereas in the peptised solution there is not this pseudomorphism and the final curd is less bulky.

The view that the peptised systems are in stage 1, *i.e.*, that they are mainly colloidally dispersed with a small amount molecularly dispersed, is supported by their optical properties. On peptisation, the Faraday-Tyndall cone becomes considerably weaker and no discrete particles can be detected ultramicroscopically.

The smallness of the temperature coefficient of the peptisation supports this view since the peptisation cannot be expected to proceed beyond the formation of primary micelles however high the temperature is raised. The results for sodium caprylate also support it since at the concentration $M/20$ where hardly any peptiser is taken up the soap is certainly still colloidal, for the most part. Sodium cerotate (C_{26}) is peptised by amyl alcohol but forms a gel on standing. This obviously requires colloidal structure. This soap is also interesting in its behaviour in ethyl alcohol. When dry it is almost insoluble in the boiling alcohol but when about 5 per cent. of water is added it dissolves readily.

No change of electrical conductivity was observed after peptisation of sodium stearate by amyl alcohol; nor was any change of p_H observed.

The work described above forms part of certain investigations undertaken for the Fuel Research Division of the Department of Scientific and Industrial Research. It was carried out in the Laboratory of Colloid Science, Cambridge, by kind permission of Professor E. K. Rideal to whom I am grateful for helpful discussions and advice.

Summary.

Aqueous soap solutions are peptised by numerous alcohols, phenols and amines, whose solubility in them is much greater than in water.

The peptised solutions are still colloidally dispersed.

There is no evidence for the existence of complexes in simple stoichiometric proportions.

For each soap and for each peptiser there is a definite saturation point which seems to be determined by the solubility of the complex. The amount of peptiser taken up at saturation varies from less than one molecule per molecule of soap to 17.

The complexes exist only in solution.

The temperature coefficient of peptisation is very small.

Complex formation seems to be by dipole interaction.

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Cambridge.

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[13] *Trans. Faraday Soc.*, 1935, 193.

A STUDY OF THE KINETICS OF AN ESTERIFICATION REACTION IN BENZENE.

By M. M. Davies.

Received 3rd November, 1936.

In investigating the kinetics of the polycondensation of ω-hydroxy-acids in benzene solution it became necessary to consider the mechanism of an ordinary esterification reaction in the same solvent. The only recently reported examination of this reaction in a non-hydroxylic solvent is that of Rolfe and Hinshelwood[1] who studied the uncatalysed interaction of methyl alcohol and acetic acid in anisole solution. The present results concern the esterification of benzyl alcohol and benzoic acid in benzene solution catalysed by *p*-toluene sulphonic acid,

$$C_6H_5CH_2OH + C_6H_5COOH \rightarrow C_6H_5COOC_6H_5CH_2 + H_2O.$$

Experimental.

Rates have been followed by heating 10 c.c. lots of solution in sealed pyrex tubes at 100° (in a boiling water bath) and at 74·3° and 137° in a well-lagged vapour bath. Experiments at the latter temperature showed the necessity of using pyrex tubes, although at 100° little difference, other than better reproducibility, is noticeable from soda-glass. Analyses were performed by adding slight excess of standard alkali and back-titrating with acid: tests with synthetic mixtures showed this method to be satisfactory. "Analar" chemicals were used, the benzene being freshly distilled from P_2O_5. Solutions were made up by volume, and in order to compare the rate constants at different temperatures the observed values were multiplied by V_t/V_{25}, where V_t is the specific volume of the solvent at $t°$. Owing to its small solubility at room temperatures, the *p*-toluene sulphonic acid used as catalyst had to be weighed (to 1/10th mg.) into each tube.

Results.

The uncatalysed reaction is extremely slow, a typical result showing 0·3 per cent. change after 48 hours at 137°. The reaction catalysed by *p*-toluene sulphonic acid is conveniently measurable at 100°, where for $N/10$ reactants it proceeds to a (homogeneous) equilibrium at 72 ± 2 per

TABLE I.—(Benzoic Acid)$_0$ = $N/2$; (Benzyl Alcohol)$_0$ = $N/2$; (*p*-Toluene Sulphonic Acid) = $N/100$.

t (hours)	3·95	6·17	14·25	23·85	41·85
Per cent. change	11·7	18·7	32·0	41·3	49·3
$k \times 10^4$	13·6	13·3	13·5	12·9	12·5

(Benzoic Acid)$_0$ = $N/10$; (Benzyl Alcohol)$_0$ = $N/10$; (*p*-Toluene Sulphonic Acid) = $N/100$.

t (hours)	6·2	7·1	15·0	16·6	22·8	23·0
Per cent. change	13·1	11·7	23·6	25·4	30·5	38·2
$k \times 10^4$	44·8	39·8	41·3	41·9	40·7	44·4

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[1] *Trans. Faraday Soc.*, 1934, **30**, 937.

cent. esterification, the latter figure varying little with temperature. The results and conclusions which follow relate to the initial stages (0-40 per cent. reaction) where the reverse reaction may be neglected.

Table I. shows some of the results for two typical series at 100°; k is the bimolecular constant expressed in (gr. mols. per litre)$^{-1}$ × mins.$^{-1}$; the percentage change is calculated on the basis of complete reaction between the benzoic acid and an equivalent amount of benzyl alcohol. It is seen that the bimolecular constant increases markedly with dilution of the reactants, the following series of initial values of k, corrected to the same total sulphonic acid concentration ($N/100$), extending this observation.

Reactants at Equivalent Concentrations	N.	$N/2$.	$N/10$.	$N/50$.	$N/100$.
$k \times 10^4$	7·7	13·5	41·5	120	480

This variation was taken to indicate that only the unassociated molecules of the reactants were concerned in the reaction. It is well-known that single molecules of benzoic acid at these temperatures exist in equilibrium with double molecules,[2] whilst the alcohols are invariably associated in hydrocarbon solvents.[3] This conclusion has been confirmed for both reactants, but before presenting the relevant experimental data, the action of the catalyst must be considered.

Experiments with *p*-toluene sulphonic acid and benzyl alcohol alone in benzene, showed that these react rapidly, reaching equilibrium after 3 hours at 100°. A precise determination of the equilibrium constant for this reaction has not been possible owing to (i) the limited solubility of the sulphonic acid—about $N/50$ at 100°, (ii) the variable water content of the solvent and of the hygroscopic sulphonic acid after handling in air, (iii) the poor end-point in the titre owing to the ready hydrolysis of the benzyl-*p*-toluene sulphonate. So pronounced is the reactivity of the latter that the ester has not yet been isolated, though its intermediate formation in various reactions cannot be doubted.[4] Accordingly, it becomes necessary to decide whether the acid or the ester is the catalytically active species. The assumption which is most consistent with the kinetic data is that the catalytic effect is proportional to the concentration of total sulphonic acid added, rather than to the estimated concentration of benzyl *p*-toluene sulphonate.

Table II. contains the results for variation of rate with catalyst concentration using $N/10$ reactants at 100°.

TABLE II.—Equivalent Concentrations of Benzoic Acid and Benzyl Alcohol = $N/10$.

(Sulphonic Acid).	$N/50$.	$N/100$.	$N/200$.	$N/500$.
$k \times 10^4$	100	41·5	19·5	7·0
$k/$ (H. Sulph) × 10^2 . .	55	41	39	35

It would be anticipated that if the ester were the more active catalytically and its concentration sensitive to presence of water, the rate should decrease considerably with the progress of reaction, especially with the higher reactant concentrations. The decreasing association of the reactants with increasing dilution, however, is a counteracting factor. Examination of the data has shown that, when allowance is made for the latter, the catalytic activity is appreciably depressed during the course of reaction. That this results from the rising water concentrations has been confirmed by comparison of the initial rates in dry benzene and in the moist solvent (saturated with water at room temperature); thus, for N-reactants, $N/100$ catalyst, initial values were $k_{(\text{dry})} = 7{\cdot}7 \times 10^{-4}$ and $k_{(\text{moist})} = 6{\cdot}7 \times 10^{-4}$.

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[2] Innes, *J.C.S.*, 1902, 682.

[3] *Inter alia*, Hennings, *Z. physik. Chem.*, *B*, 1935, **28**, 267.

[4] Lapworth, *J.C.S.*, 1912, **101**, 273.

In order to follow the variations in rate with degree of association of benzoic acid, series of experiments were performed with constant initial alcohol concentration ($N/10$). In Table III., k is the mean value of the initial bimolecular rate constant for the reactant concentrations specified.

TABLE III.[*]—(BENZYL ALCOHOL)$_0$ = CONSTANT = $N/10$.

(Benzoic Acid)$_0$.	(Sulphonic Acid).	$k \times 10^4$.	k (H. Sulph.) $\times 10^2$.	$K_{(\text{HBz})}$.
$N/5$	$N/100$	30·0	30·0	0·033
$N/10$	$N/100$	41·5	41·5	0·037
$N/20$	$N/100$	57·7	57·7	0·044
$N/50$	$N/400$	18·4	73	0·038
$N/100$	$N/500$	17·0	87	0·038

[*] In this table and hereafter p-toluene sulphonic acid is for brevity designated (H. Sulph.) and benzyl alcohol and benzoic acid, respectively, BzOH and HBz.

It is now assumed that the figures in column 4 are proportional to the fractions of benzoic acid (α) in the monomeric form; whence by taking the limiting value of 120 for infinite dilution (*i.e.*, $\alpha = 1$), the association constant $K_{(\text{HBz})} = \dfrac{2c\alpha^2}{1 - \alpha}$, is found to have the values in column 5. Possibly the best estimate that can be made of this constant at 100° from previous data is by extrapolation of Innes' results,[2] based on boiling-point elevations. Recalculation from his molecular weights gives an unsatisfactory $\log K_{(\text{HBz})} \sim 1/T$ plot, but suggests a value at 100° probably within the range $0{\cdot}10 \sim 2{\cdot}7$. It is not clear whether the discrepancy is due to the limitations of the present treatment or to incorrect evaluation of molecular weights by Innes, *cf.* the molecular weights of benzoic acid reported by Bury and Jenkins [5] and by Auwers [6] at the freezing-point in benzene.

Table IV. shows the variation of k with alcohol concentration, the benzoic acid being of initial concentration $N/10$ throughout.

TABLE IV.—(BENZOIC ACID)$_0$ = CONSTANT = $N/10$.

(Alcohol)$_0$.	(Sulphonic Acid).	$k \times 10^4$.	k (H. Sulph.) $\times 10^2$.	$K_{(\text{BzOH})}$.
$N/5$	$N/100$	36	36	$0{\cdot}14_7$
$N/10$	$N/100$	41·5	41·5	$0{\cdot}11_3$
$N/20$	$N/100$	55	55	$0{\cdot}15_3$
$N/50$	$N/200$	38	76	0·72
$N/100$	$N/200$	23	46	$0{\cdot}01_8$

The figures for the association constant of benzyl alcohol in the final column are based upon a value of $k/$(Sulph.) $\times 10^2 = 80$ for $\alpha = 1$.

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[5] *J.C.S.*, 1934, 688.

[6] *Z. physik. Chem.*, 1896, **21**, 337.

Whilst association of the alcohols is certainly not limited to dimerisation [7] it seems probable that at the temperature and concentrations considered, the process does not proceed beyond this stage.

The foregoing scheme can now be tested by using the results for equivalent reactants at different concentrations quoted earlier. We should have $k_{(\mathrm{obs.})} = k(\mathrm{catalyst})\ \alpha_1\alpha_2$ where α_1 and α_2 are the fractions as simple molecules of acid and alcohol respectively. Table V. summarises the calculations made with the association constants previously evaluated: ($K_{(\mathrm{HBz})} = 0{\cdot}038$; $K_{(\mathrm{BzOH})} = 0{\cdot}15$).

TABLE V.

$(\text{Benzoic Acid})_0 = (\text{Benzyl Alcohol})_0$.	(Sulphonic Acid).	$k_{(\mathrm{obs.})} \times 10^4$.	$\dfrac{k_{(\mathrm{obs.})}}{\text{H. Sulph. } \alpha_1\alpha_2}$.
N	$N/100$	7·7	2·51
$N/2$	$N/100$	13·5	2·38
$N/10$	$N/100$	41·5	2·08
$N/50$	$N/300$	39·5	2·37
$N/100$	$N/300$	100	7·51

Considering the large variation in $k_{(\mathrm{obs.})}$, the constancy of all but the last figure in the final column is satisfactory. We may therefore take the "best" value, 2·45, as the velocity constant for the termolecular process involving ($C_6H_5 . CH_2OH$) monomer, ($C_6H_5 . COOH$) monomer, and $p . CH_3 . C_6H_4SO_3H$.

Table VI. summarises the results at 137° for those concentrations which have been examined in detail. The values of α_1 and α_2 at 137° have been calculated from the following association constants at this temperature: $K_{(\mathrm{HBz})} = 0{\cdot}49$; $K_{(\mathrm{BzOH})} = 0{\cdot}24$. These were evaluated from their values at 100° and heats of association of 21,000 cals./mole. and 4000 cals/mole respectively. The former value of ΔH is that suggested by the slope of the plot of Innes' data, whilst the latter is that reported for a series of aliphatic alcohols in benzene by Wolf, Pahlke, and Wehage.[8]

TABLE VI.

Concentrations.	(Sulphonic Acid).	$k \times 10^3$.	$k/$ (H. Sulph.).	$\dfrac{k}{\text{H. Sulph. } \alpha_1\alpha_2}$.
$N/10 : N/10$ . .	$N/100$	13·6	1·36	2·76
$N/50 : N/50$ . .	$N/500$	$4{\cdot}3_7$	2·18	2·70
$N/50$ alc. $N/10$ acid .	$N/300$	$5{\cdot}8_5$	1·75	2·62
$N/50$ acid : $N/10$alc. .	$N/300$	$5{\cdot}3_4$	1·60	2·68

Table VII. similarly summarises the less extensive results at 74·3°.

TABLE VII.

(Concentrations).	(Sulphonic Acid).	$k \times 10^4$.	$k/$ (H. Sulph.) $\times 10^2$.	$\dfrac{k}{\text{H. Sulph. } \alpha_1\alpha_2}$.
$N/10 : N/10$ . .	$N/100$	12·3	12·3	1·64
$N/50 : N/50$ . .	$N/400$	9·4	37·6	1·68
$N/50$ acid : $N/10$ alc.	$N/400$	6·0	24·0	1·60

The values of α_1 and α_2 were calculated on the same basis as those at 137°

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[7] Brown and Bury, *J. Physic. Chem.*, 1926, **30**, 694, and Hennings.[3]

[8] *Z. physik. Chem.*, *B*, 1935, **28**, 1.

It thus seems that the foregoing scheme is consistent within itself, and a kinetic activity proportional to the monomer concentration appears to be established.

Up to the present, we have considered the association of the benzoic acid and of the benzyl alcohol, but no possible interaction of a like nature between these species. The formation of a complex between monomeric acid and alcohol, if it occurred, would probably be an important element in the kinetic mechanism. Accordingly, an attempt was made to trace the formation of such a complex, with positive results. The method consisted in determining the partition ratio of benzoic acid between water and benzene on the one hand, and water and a benzene solution of benzyl alcohol on the other. Both series were run concurrently and, at 20·5°, the partitions coefficients were determined with both $N/5$ and $N/10$ solutions of benzyl alcohol; at 60·8° only the higher concentration of alcohol was used. From the results for the simple benzene-water partition, by using the water phase as reference, the concentration of benzoic acid present as complex in the benzyl alcohol solution could be evaluated. In calculating the equilibrium constant for the interaction

$$C_6H_5.COOH + C_6H_5.CH_2OH \rightleftharpoons C_6H_5.COOH.C_6H_5.CH_2OH.$$

$$K_{(\text{complex})} = \frac{(\text{Complex})}{(C_6H_5.COOH)(C_6H_5.CH_2OH)}$$

knowledge of the association constants for acid and alcohol at the temperatures at which distribution measurements were made becomes necessary. These have been estimated from independent data: for the alcohol from $K_{(\text{BzOH})} = 0{\cdot}6$ at 20°, and $\Delta H = 4000$ cals, the former figure being suggested by Auwers' molecular weight data at the freezing-point;[9] whilst for the acid Hendrixson's partition results at 10°[10] give a very steady association constant for benzoic acid in benzene saturated with water, *viz.* $K_{(\text{HBz})} = 0{\cdot}028$.* The mean of eight reasonably consistent values at 20° gives $K_{(\text{complex})} = 3{\cdot}5 \pm 0{\cdot}5$, with a heat of formation $-\Delta H \sim 6000$ cals./mole.

If c_1 and c_2 are the total concentrations (expressed in terms of monomer) of the acid and alcohol independent of their molecular state; γ = conc. of the acid-alcohol complex; α_1 and α_2 the fraction of free acid and alcohol as monomers,

$$K_{(\text{complex})} = \frac{\gamma}{(c_1 - \gamma)(c_2 - \gamma)\alpha_1\alpha_2}.$$

If only the acid-alcohol complex is kinetically active, the rate equation should be written

$$\frac{dx}{dt} = k_0(\text{complex})\,(\text{H. Sulph.}) = k_0(\text{H. Sulph.})K_{(\text{complex})}(c_1 - \gamma)(c_2 - \gamma)\alpha_1\alpha_2.$$

This will differ from the rate equation previously adduced for the mechanism,

$$C_6H_5.\ COOH_{(\text{monomer})} + C_6H_5.CH_2OH_{(\text{monomer})} + \text{H. Sulph.}$$
$$\rightarrow \text{Ester} + H_2O + \text{H. Sulph.}$$

viz.

$$\frac{dx}{dt} = k'(\text{H. Sulph.})c_1c_2\alpha'_1\alpha'_2$$
$$= k_{(\text{obs.})}c_1c_2,$$

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[9] *Z. physik. Chem.*, 1893, **12**, 689. [10] *Z. anorg. Chem.*, 1897, **13**, 73.

* There is a strong indication in the case of benzoic acid that its association in benzene is considerably reduced by presence of water. Thus, freezing-point data and Innes' boiling-point data at 54° indicate virtually complete dimerisation, whilst Hendrixson's well-substantiated figures (at 10°) show (monomer) > 15 per cent. for N solution. The same influence of water is probably manifested in the frequent difference of the experimentally determined partition-constant and the ratio of the solubilities in the individual solvents. (See Brown and Bury.[7])

only if γ is an appreciable fraction of c_1 or c_2. The values of $K_{(\text{complex})}$ show that it is impossible to distinguish between these possibilities from the kinetic data.

A plot of log $k' \sim \frac{1}{T}$ indicates a maximum value of E ~ 3500 cals. per mole., for the activation energy of the second mechanism.

Discussion.

The dependence of the reaction upon the monomeric species of the reactants seems to be well-established. This is in contrast with the conclusion of Rolfe and Hinshelwood[1] that, in the uncatalysed methyl alcohol-acetic acid reaction in anisole, the dimeric acid molecule is an effective reactant species when catalysed by the monomer.

Although the results have been treated as establishing a rate proportional to the total sulphonic acid concentration this does not eliminate the possibility that the reaction proceeds via the benzyl sulphonic ester. The conditions in the mixed solution might easily be such as to reduce the latter's concentration to a linear dependence upon the total acid. The labile nature of the sulphonic ester would then explain the unique catalytic activity of this acid as compared with perchloric, hydrobromic and picric acids, all of which apparently react with the alcohol but have little catalytic activity. It is interesting to note that

$$K_{(\text{Bz Sulph.})} = \frac{(\text{C}_6\text{H}_5\,.\,\text{CH}_2\text{Sulph.})\,(\text{H}_2\text{O})}{(\text{C}_6\text{H}_5\text{CH}_2\text{OH})\,(\text{H. Sulph.})}$$

was estimated to have a value at 100° = $1{\cdot}0 \pm 0{\cdot}3$ whilst $-\Delta H$ the heat of formation of the ester ~ 5000 cals./mole. These figures support the foregoing remarks as to its possible behaviour.

Summary.

The kinetics of the benzyl alcohol-benzoic acid esterification, catalysed by *p*-toluene sulphonic acid, has been examined in benzene solution at 74·3°, 100°, and 137°. The results are consistent with the view that only the monomeric molecules of the reactants are kinetically active. The action of the catalyst is discussed.

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THE SURFACE STRUCTURE OF SILICON CARBIDE.

By G. I. Finch and H. Wilman.

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Surfaces of mercury, fused silica, glass and the polish layer on metals, all interact with the electron beam at grazing incidence to give a pattern consisting of diffuse scattering through which a broad ring (or rings) is more or less faintly visible. In the case of mercury and polished metal surfaces the radii of these halos correspond to the mean distance of approach of the atoms, *i.e.*, to the atomic diameter, but with molecular vitreous substances like glass they are in the main functions of the atomic separations within the chaotically distributed molecules. The electron diffraction halo pattern is now widely accepted as evidence of an amorphous structure, as distinct from the crystalline.

Recently L. H. Germer [1] obtained the halo pattern from the surfaces of silicon carbide plates. Since, however, these plates are quite obviously crystalline, their larger and exceedingly smooth and flat surfaces being immediately recognisable from the external crystal shape as basal planes, he concluded that this fact vitiated the usual interpretation of the halos as set forth above. On the other hand, one might, it seems to us, equally well construe Germer's results as evidence of the existence of an amorphous layer covering the carborundum crystal, and of such thickness as to prevent access of the electron beam to the underlying crystal. The issue is one of great importance which we have put to the test of experiment, to find as a result that the halo pattern from the carborundum crystal is indeed due to a vitreous skin.

Experimental.

Transparent, colourless or only slightly green crystal plates of carborundum can be freed easily from the commercially obtainable magma without injuring the prominent basal planes. Four such plates were chosen for these experiments. Their free basal plane surfaces were optically smoother than any natural or cleavage single crystal face which we have so far seen, and were indeed so perfect they might well be described as having the appearance of a high degree of polish. Furthermore, in superficial area these plates ranged between about 0·25 and 0·5 cms.^{2}, a size which experience has shown to be an optimum for the purpose of diffraction of electrons at grazing incidence by single crystals. Nevertheless, from all parts of their natural faces, these crystals gave nothing but the halo pattern, a result which is in complete agreement with that obtained by Germer.

Acheson,[2] however, has noted the presence of oxidation products, such as silicon oxycarbides, in the zone of the so-called amorphous carborundum which in the electric furnace surrounds the pure well-crystallised product. It seemed to us possible that a skin of similar material, or even of silica, might well have been formed on the crystals as a result of seepage of air and products of combustion of carbon into general contact with the charge during cooling. We found, in fact, that the presence of such a film was indicated by interference colours on some of our crystals. Accordingly, we rubbed one of the carborundum crystals on moist emery paper (Hubert No. 000), the abrasive on which consists mainly of alumina and rouge, and is therefore softer than carborundum but harder than silicon. After washing to remove all traces of abrasive and adventitious grease, this crystal surface afforded brilliant single crystal patterns of carborundum. That shown in Fig. 1 was repeated on rotation in the azimuthal plane at intervals of 120° ; thus confirming the surface as being the basal plane of the hexagonal crystal, the azimuthal setting for this pattern being such that the beam was parallel to a (110) type of plane.

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[1] L. H. Germer, *Physic. Rev.*, 1936, **49**, 163.

[2] E. G. Acheson, quoted by J. W. Mellor, *A Treatise on Inorganic and Theoretical Chemistry*, Longmans, Green, London, 1924, **5**, 884.

A fresh crystal which had previously given a halo pattern was now immersed in a hydrofluoric acid solution for two minutes. Carborundum is not attacked by this acid. After washing, this crystal also yielded brilliant patterns similar to Fig. 1 from all over the surface. It was then heated rapidly to white heat for a few seconds in an oxy-coal-gas flame, and this treatment was found to have restored the crystal to its former condition, in that it once more yielded a halo pattern of the original type, no vestige of the single crystal pattern being anywhere obtainable. The surface was now restored, by rubbing on emery paper, to the condition in which it gave clear sharp single crystal patterns, whereafter it was raised quickly to a bright red heat in an oxidising Bunsen flame. This time it yielded a pattern (Fig. 2) consisting of Kikuchi lines showing only faintly through the intense background scattering of the halo type of pattern. Boiling the crystal in this state in a concentrated potassium hydroxide solution, followed by several washings with hot distilled water, restored the surface to the condition in which it once more gave bright single crystal patterns. Further experiments with the other crystals, in which the sequence of operations outlined above was varied, gave similar results. A feature worthy of note is the fact that throughout all these treatments the crystal surfaces retained their smoothness and general reflecting properties practically unimpaired.

Discussion.

In the light of these results it is now easy to see why the raw, untreated carborundum crystal yields the halo type of pattern. In such a surface the carborundum crystal structure is, in fact, hidden from the electron beam by a layer of amorphous material which gives rise to the halos. This amorphous material appears to be a silica film in the vitreous state, because as we have shown, it is much softer than carborundum, is soluble in hydrofluoric acid and in strong alkali, and it is formed by superficial oxidation at temperatures which lie far below the fusion point of carborundum, but within the range of softening of silica.

The mild temperature of oxidation in the Bunsen flame which brought about the surface condition giving rise to Fig. 2 evidently produced a silica film which was so thin as to be only partially opaque to the electrons, so that vestiges of the single crystal pattern are still in evidence through the incoherent background in Fig. 2. Some idea as to the upper limit of thickness of the amorphous film in this case can be obtained as follows :

The angle of incidence of the grazing beam upon the crystal face was about 2°. Thomson,[8] calculates a mean-free-path of 4×10^{-6} cms. for 30 KV. electrons to lose energy by ionisation of the atoms in a solid. Thus the maximum thickness of the amorphous layer formed on heating

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[8] G. P. Thomson, *Phil. Mag.*, 1934, 18, 640.

1.—Single crystal pattern from carborundum after removal of the amorphous skin which otherwise so obscures the crystal surface that only the halo pattern is obtained.

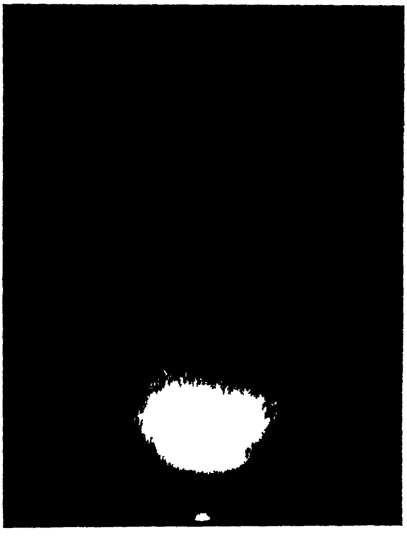

FIG. 2.—Single crystal pattern showing faintly through halo and background scattering due to very thin amorphous skin formed by oxidation in a Bunsen flame.

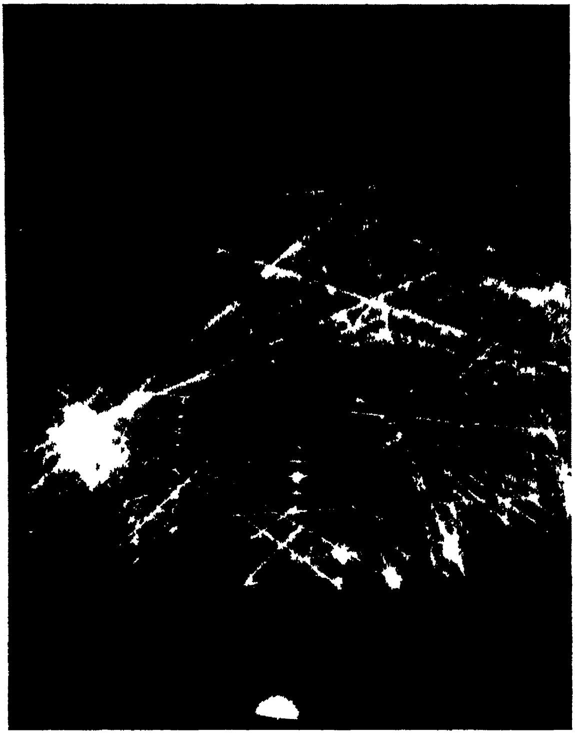

FIG. 3.—Pattern from the curved surface of a quartz single crystal cut and polished as a plano-convex lens.

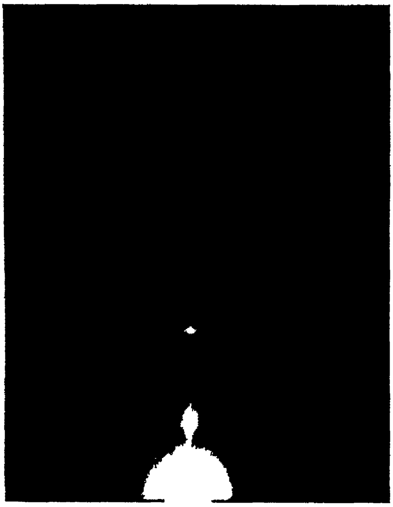

FIG. 4.—Pattern from a mono-molecular $C_{32}H_{66}$ film completely obscuring the quartz single crystal substrate.

[*To face page* 339

in the Bunsen flame and semi-transparent to our electron beam must have been of the order of 30/2 = 15A, because the electrons coherently scattered by the crystal structure must again pass through the amorphous layer on their way to the screen. We have also confirmed the correctness of the order of this estimate by the following direct experiment.

A polished plano-convex quartz lens of 1·5 cms. radius cut from a single crystal was examined in the camera and found to give excellent single crystal patterns of bright spots and sharp Kikuchi lines in all azimuths from every part of its curved surface (Fig. 3). Sufficient alcohol-ether solution of $C_{32}H_{66}$ to give on drying a single layer of closely packed erect molecules was dried out on the convex surface. Fig. 4 is representative of the patterns then obtained from all over the lens. This pattern is wholly characteristic of the unimolecular paraffin film, and completely obliterates any trace of diffraction by the quartz. Thus, from this result we can infer directly that the thickness of the amorphous film on the carborundum crystal yielding Fig. 2 must have been much less than 43A.

Summary.

It has been shown experimentally that the electron diffraction halo pattern obtained from carborundum crystals is due to a superficial skin consisting in all probability of amorphous silica. Removal of the skin by abrasion or by quartz-etching reagents exposes the true carborundum crystal surface which then yields brilliant single crystal patterns. The skin is reformed by heating in an oxidising flame. Such an amorphous layer formed in a Bunsen flame was sufficiently thin to be semi-transparent to 50 KV. electrons, the crystal giving a composite halo-single-crystal pattern. From this and the further experimentally established fact that a monomolecular layer of $C_{32}H_{66}$ is not fully penetrated by electrons of this speed at grazing incidence, it has been shown that the semi-transparent amorphous film was less than 43A in thickness.

We wish to thank the Department of Scientific and Industrial Research and Messrs. Ferranti Ltd. for grants and apparatus, Mr. F. D. Zahoorbux for assistance with the paraffin film experiments, and Dr. J. C. Smith, who supplied the pure paraffin.

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THE ABSORPTION SPECTRA AND PHOTO-SENSITISING ACTIVITY OF WHITE PIGMENTS.

By C. F. Goodeve.

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The action of zinc oxide in photosensitising the decomposition of organic compounds and a number of inorganic reactions, has long been known. In this connection the experiments of Eibner,[1] Winther,[2] and Baur and co-workers,[3, 4] are outstanding.[5]

The action of titanium dioxide in discolouring dyestuffs has been described by Keidel [6] and by Wagner.[7] Both these authors found that dyes which are quite stable to light when adsorbed on Lithopone or white lead, are rapidly decomposed when in contact with titanium dioxide and sometimes with zinc oxide. Wagner ascribes the action of TiO_2 to the presence of sulphuric acid. Wagner and Zipfel [8] found that zinc oxide can reduce the action of titanium dioxide with certain dyes. Renz [9] has described the photo-reduction of titanium dioxide in the presence of glycerine.

In the present paper, the results of measurements of the absorption spectra of some of the common white pigments are given, and possible mechanisms for the photochemical activity are discussed.

Photochemical Properties of White Pigments.—It is not intended to give here a complete review of the many experiments described in the literature. In most cases these experiments were carried out during a period in which the importance of the wave-length of the light used was not appreciated, and usually the wave-length was not specified. In general, however, the results show that it is the ultra-violet part of the spectrum which is active. In the case of zinc oxide, activation was caused by light from a mercury arc, filtered through glass, thus indicating that the near ultra-violet (above 330 mμ) is able to activate this substance. This fact has been confirmed by a number of experiments carried out by the author. It has also been shown that the same is true for titanium dioxide. Usually dyes attacked by ZnO were not attacked so much by TiO_2 and vice versa.

In the case of white lead, there seems to be no evidence of sensitising activity by the ultra-violet from the sun (down to 300 mμ). From the results of Winther [2] it can be concluded that there is an activity for light below this wave-length.

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[1] A. Eibner, *Chemiker Zeitung*, 1911, 753, 774 and 786.

[2] Chr. Winther, *Z. wiss. Photo.*, 1921, **21**, 141, 168 and 175.

[3] E. Baur, *Helv. Chim. Acta*, 1918, **1**, 186.

[4] E. Baur and C. Neuweiler, *ibid.*, 1927, **10**, 901.

[5] An excellent summary of the subject has been made by A. Perret, *J. Chimie Physique*, 1926, **23**, 97. Brief descriptions of most of the results are to be found in all text-books on Photochemistry, a long list of references being given in *Allgemeine Photochemie*, 1936, p. 634, by J. Plotnikow.

[6] E. Keidel, *Farben Zeitung*, 1929, **34**, 1242.

[7] H. Wagner, *ibid.*, 1929, **34**, 1243.

[8] H. Wagner and M. Zipfel, *ibid.*, 1932, **37**, 1480.

[9] C. Renz, *Helv. Chim. Acta*, 1921, **4**, 961.

Lithopone is apparently not a good photosensitiser but often itself decomposes. Pfund[10] found that the light below 360 mμ was alone active in this respect.

Barium sulphate has been found[11] to be photochemically inactive.

The sensitised oxidation of water by oxygen in the presence of zinc oxide, as found by Baur and Neuweiler,[4] is a particularly interesting example of the activity of this latter substance. Their results have been confirmed by experiments carried out by the author. Attempts to repeat the experiment with titanium dioxide were, however, unsuccessful. Winther's claim[12] to have found ozone produced by the illumination of zinc oxide in the presence of oxygen has been discredited by the results of McMorris and Dickinson.[13]

The " chalking " of paints made with titanium oxide is well known,[14] but the question as to whether it is caused by photochemical action has not been settled.[15] Gussjatzkaja[16] apparently believes that " chalking " is caused by a thermal catalysis, involving titanium dioxide. Pfund[10] considers that " chalking " is mainly due to decomposition of the oil vehicles. Addition of zinc oxide reduces " chalking."[17] Heise[18] believes that this is due to the formation of zinc soaps with the linseed oil. These soaps, incidentally, have been found by the author to be effectively transparent in the near ultra-violet.

Attempts have been made by the author to test these points by the use of filtered light from the sun and from a mercury arc. The results were not conclusive and showed only the extreme difficulty of obtaining suitable blanks with identical conditions of humidity, temperature, etc.

The author has also sought to test for gaseous products of photodissociation of pure dry TiO_2 and ZnO. Quantities of the material were sealed in a flat quartz vessel, baked out to 100° C. under a high vacuum for three hours and then illuminated with a mercury arc for forty-eight hours. In neither case was a detectable amount of permanent gas found to be evolved. So far as one is able to calculate from inadequate thermal data, the production of oxygen is unlikely except in the extreme ultra-violet.

Previous Attempts at Measuring Absorption Spectra of White Pigments.—Winther[2] studied the light absorption of a number of substances in the ultra-violet by their effect in reducing the fluorescence of mercurous chloride with which they were intimately mixed. He gives a curve for zinc oxide with a maximum at 366 mμ and a minimum at about 300 mμ. The intensity of fluorescence from such a mixture is bound up with the absorption coefficients of *both* substances, and the minimum indicated by Winther was more likely due to the rapid increase in absorption by mercurous chloride found by him for the same region.

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[10] A. H. Pfund, *Proc. Am. Soc. Test. Mat.*, 1923, **23** II., 369.

[11] H. A. Gardner, *Physical and Chemical Examination of Paints, etc.*, 1935, p. 235.

[12] Chr. Winther, *Z. wiss. Photo.*, 1921, **21**, 168 and 175.

[13] J. McMorris and R. G. Dickinson, *J.A.C.S.*, 1932, **54**, 4248.

[14] A series of papers on chalking by R. Kempf is to be found in recent numbers of the *Farben Zeitung*.

[15] See for example a discussion on a paper by D. Wait, " Titanium Pigments," *J. Oil and Colour Chemists Assn.*, 1935, **18**, 143.

[16] L. W. Ljutin and E. V. Gussjatzkaja, *J. Appl. Chem. Russ.*, 1935, 8, 833.

[17] See K. Heise, *Titanweiss*, 1936, p. 42.

[18] K. Heise, *ibid.*, p. 71.

Attempts have been made to measure the absorption spectra by studying the transmitted light of a number of solid inorganic powders by Kimura and Takewaki.[19] The powders were placed in a wedge-shaped quartz cell. They state that zinc oxide cuts off the ultra-violet sharply whereas aluminium oxide does not. The author has tried to repeat these observations, but without success. It has not been found possible to make sure that the light entering the spectroscope has actually passed through the particles and the effect was complicated by the variation of scattering with wave-length (Rayleigh effect).

The transparency of various pigments made up in the form of paints has been determined by Pfund,[10] Hallett,[20] and Stutz.[21] The most extensive work was done by Stutz who used an integrating sphere to collect the whole of the light which passed through the paint film. Practically all of the common pigments were tested. While his results are of considerable interest in themselves, the actual values obtained would be difficult to reproduce because of their dependence upon particle size, amongst other factors. Stutz also studied the transmission of mixtures of zinc oxide and basic lead carbonate. His results show no indication of a maximum of absorption at 365 $m\mu$ as found by Winther.

The Diffuse Reflection Method.—Light diffusely reflected from white powdered pigments is scattered completely at random and obeys the cosine law. Only a small part of this light has been reflected from the front surfaces of the crystals of the powder; the larger part has passed through a number of crystals and finally emerges from the surface. Most coloured pigments have "body-colour," that is, certain wave-lengths are absorbed on transmission through the crystals. This is the case for practically all coloured pure substances.

The intensity of the light reflected from air-solid interfaces is a function of the refractive index and accordingly increases with decreasing wave-length. On the classical theory, the chance of a quantum of light being reflected from a flat surface decreases if the size of that surface is reduced much below the wave-length of the light. For a distribution of particle sizes the chance should, therefore, increase with decreasing wave-length. Neither of these effects is large, otherwise "white" pigments would appear bluish.[22]

A large *decrease* in the intensity of the diffusely reflected light with change of wave-length must be due to the presence of an absorption band in the solid. A study of the diffuse reflection spectra affords, therefore, a method of determining the position of this band.

Wood [23] was one of the first to recognise that zinc oxide is "black" in the ultra-violet. Pfund [10] and Stutz [24] measured the diffuse reflecting power of coloured and white pigments for the ultra-violet lines of the mercury arc and ascribed the low values for some of these to the presence of absorption bands. Luckiesh [25] has published curves of the reflecting power for a large number of substances but gives no details of his experimental methods or of the purity of his materials, etc. Some of his curves are reproduced in Fig. 2, together with observations by Pfund and by Stutz. The use of a discontinuous light source such as the mercury arc has limitations in so far as it is impossible to find the threshold of the absorption band. Luckiesh's curves indicate considerable absorption by silica and magnesium carbonate at 300 mμ. Such absorption is not to be expected from these substances and its existence has not been confirmed in the present work.

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[19] M. Kimura and M. Takewaki, *Sci. Pap. Inst. Phys. Chem. Res.*, 1928, **9**, No. 155, p. 57.

[20] R. L. Hallett, *Proc. Am. Soc. Test. Mat.*, 1923, **23** II., 379.

[21] G. F. A. Stutz, *J. Frank. Inst.*, 1926, **202**, 89.

[22] Freshly precipitated white substances often do appear bluish.

[23] R. W. Wood, *Roy. Inst. Proc.*, 1913, **20**, 180.

[24] G. F. A. Stutz, *J. Frank. Inst.*, 1925, **200**, 87.

[25] M. Luckiesh, *J. Opt. Soc. Am.*, 1929, **19**, 10.

Experimental Technique.

Coblentz [26] studied the diffuse reflecting power of various white pigments by means of a hemispherical mirror and thermopile arrangement. In this the total radiation scattered by the powder is measured and compared with the intensity of the incident radiation. Variations of wave-length were obtained by the use of filters. The use of this method in the ultra-violet, however, involves great difficulties.

In this research a photographic technique, similar to that used by Pfund, was employed. Light from a hydrogen discharge tube (continuous in the U.V.) was allowed to fall on the flat surface of the dry powder at an angle of 45°, as shown in Fig. 1. The flat surface was produced by pressing the powder gently into its container and scraping the surface to remove any glaze. The reflected light then passed through the slit of a large-aperture spectrograph (Hilger E. 420) and was photographed after dispersion, using Wellington Ortho process plates (medium grained).

The chief difficulty in this method of measurement lies in obtaining a suitable standard for comparison.[27] The reflecting power of practically all substances examined appeared to fall slightly with decreasing wave-length when they were compared with the *direct* rays of the hydrogen tube. Such a comparison is not free from objection as the distribution of the light over the aperture of the spectrograph is necessarily different in the two cases. A matted quartz plate could not be used as its diffuse reflecting power varies considerably with wave-length.[28] For the purpose of this work, however, it was found possible to use a totally reflecting quartz prism. This was rotated into position as shown in the figure. The intensity of the light from the prism was reduced by means of a rotating sector. The spectrum of this light was matched on the photographic plate with that from the surface of the powder. The reflecting power was calculated relative to that at 436 mμ where it has been taken as 90 per cent. for all white materials. This is the average reflecting power for these substances and the variations from this value are not important for the present purpose. Small corrections had to be made between 300 and 250 mμ to bring the results relative to the direct beam. Beyond this latter point these corrections became unreliable. Wave-lengths were measured by comparison with a mercury arc.

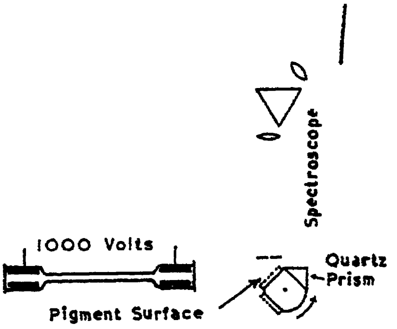

Fig. 1.

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[26] W. W. Coblentz, *Bull. Bur. Stand. Wash.*, 1912, 9, 283.

[27] Magnesium oxide as used by Pfund can only be a sub-standard and indeed this standard has been found by L. J. Wood (*unpublished*) to be unreliable in the ultra-violet.

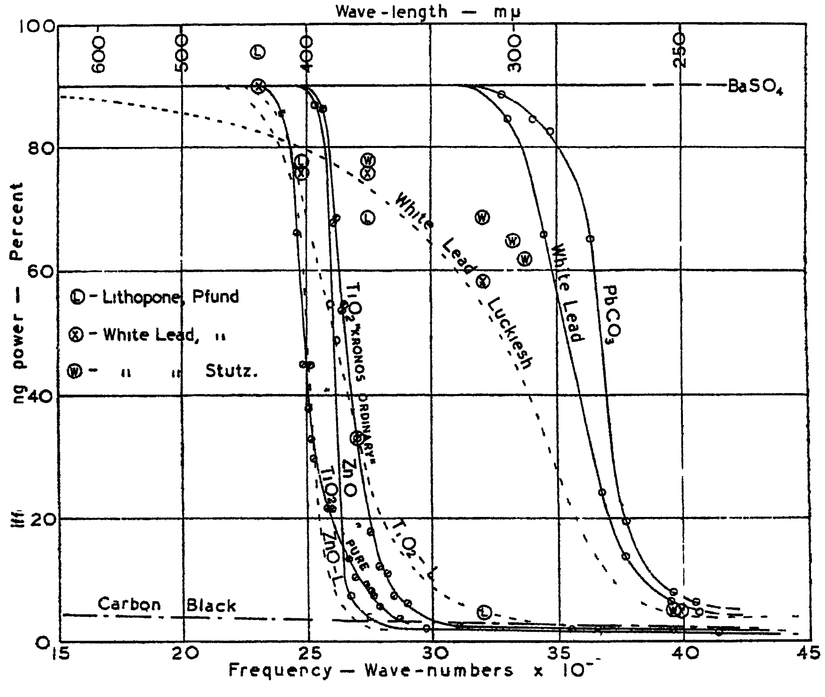
[28] See R. W. Wood, *Physical Optics*, 1934, p. 40.

Materials.

The titanium dioxide used for these experiments was 99·9 per cent pure, kindly prepared for us by British Titan Products, Ltd. Measurements were also made on "Kronos Ordinary," 97·5 per cent. pure, and on other samples prepared by precipitation from the purer specimen. The zinc oxide A.R., lead carbonate and barium sulphate were supplied by Hopkins and Williams, Ltd. The white lead was a commercial product of good quality.

Results.

The results of measurements for one sample of each substance are shown in Fig. 2, in which the diffuse reflecting power is plotted against the frequency of the light. Curves for a number of samples of zinc and titanium oxides were obtained and showed minor differences to those shown, depending largely upon their heat treatment, purity etc. Some had a brownish colour indicating that the absorption band had been shifted towards the visible. Cooling in liquid air made no detectable change in the curves.



It will be observed from the figure that in the case of pure titanium dioxide and zinc oxide there is a very sharp fall in the reflecting power at 400 mμ and 385 mμ respectively. The fall with zinc oxide is much more abrupt than that with titanium dioxide, and in both cases the curves are steeper than those given by Luckiesh. This might be taken to indicate that he used a wide range of wave-lengths for each measurement. The curves for these two oxides become flat again at a reflecting power of about 2 per cent., and remain unchanged so far as the observations extend. Lead carbonate retains its high reflecting power until 300 mμ after which it falls to a low value. The reflecting power of a sample of carbon black is shown for comparison (the reflecting power of various samples varies considerably). It will be seen that in parts of the spectrum the above substances are " blacker " than carbon black.

Barium sulphate retains its reflecting power to the limit of the observations. This was also found to be the case with aluminium oxide, precipitated silica and magnesium carbonate.

Discussion.

For reasons given above the rapid fall in reflecting power of three of the above substances indicates the entry of a strong absorption band with a fairly sharp threshold. The light of wave-length below this threshold, reflected from the powders, undoubtedly comes from the front surfaces of the particles—this accounting for the flatness of the curves. The positions of the thresholds together with the minimum size of the quantum of light absorbed by various substances are shown in the table opposite.

	Approximate Threshold Wave-length.	Minimum Quantum
	m .	cals.
Titanium dioxide (pure)	400	71,000
Zinc oxide . . .	385	74,000
Lead carbonate . .	274	104,000
Lithopone (Pfund) .	351	81,000

It will be seen from the table and Fig. 2 that titanium and zinc oxides absorb light in the near ultra-violet whereas lead carbonate and white lead absorb only in the region beyond the limit of sunlight 290 mμ. These are exactly the regions in which these substances are photoactive. With the lithopone used by Pfund the rise of activity of discoloration was found to occur in the same wave-length region as the rise in absorption, a fact which he probably intended to point out. The fact that no absorption was found for substances which are not photoactive, extends the correlation. Carbon black is apparently an exception, no evidence of photoactivity arising from its strong absorption having been recorded. Such may exist but be difficult to detect.

It would be of interest from a theoretical point of view to know whether the absorption spectrum of these substances is continuous or discontinuous. This cannot be determined by the above method since, if their extinction coefficients rise to the usual maximum value (10^{-16} cm.^{2} per molecule), a particle 0·01 μ would absorb effectively all of the light which enters it. Variations in the top part of the extinction coefficient curve would not, therefore, have any effect on the reflecting power curve. Smaller particles would allow the light to penetrate still deeper. On the whole, however, it can be said that the slope of the threshold is consistent with a continuous type of absorption. In a subsequent communication it is proposed to show the relation between the absorption of some of these pigments and that of their ions in solution.

The next stage is a consideration of the mechanism of the process and the factors which govern its efficiency. A precipitated powder consists of agglomerates of submicroscopic crystals. A quantum of light energy when absorbed by an electron in such a crystal is probably initially localised (in the case of non-conductors). Before it can cause a photochemical change, this energy must pass as a more or less complete unit (Frenkel [29] has termed this unit an " exciton ") to the point of contact of the potentially reactive molecular species. In the case of carbon black, or metallic blacks (conductors), such a transfer is exceedingly unlikely to occur owing to the disturbance of the "free" electrons which would lead to degradation of the "exciton" to heat. In a pure crystal of a non-conductor an excited electron is only influenced by electrons of neighbouring molecules and there is very little coupling with the vibrations of the atoms and molecules. Degradation to heat is, therefore, less likely to occur than with carbon black. Two things may happen. The "exciton" may be reradiated as fluorescence of the same or a lower frequency, or it may be passed to a neighbouring electron by resonance between the two. The probability of the transfer of energy between two electrons of identical frequencies separated by the distances occurring in crystals is high. We have, therefore, as a picture of the probable state of affairs subsequent to absorption of a light quantum—a rapid passage of the exciton at random throughout the crystal until it meets a surface where it might cause a chemical change.

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[29] J. Frenkel, *Physik. Z. der Sowjetunion*, 1936, 9, 158.

The "exciton" here is pictured as an excited electronic state, the energy being handed on without actual transfer of the electrons. It may, however, be of the type of excitation found in some photoconductive crystals,[30] in which an ion pair is formed on absorption of light. The position of the ions (not the ions themselves) may move to the surface, causing oxidation or reduction.

There appear to be two other possible explanations. It may be that only light quanta absorbed by molecules in the surface layer can cause a chemical change and that they do this with a high efficiency. Alternatively, light quanta absorbed in the centre of a particle may move about until they reach the surface, not by resonance transfer but by re-emission and absorption in another part of the particle.[31] The experimental data and the present theory are insufficient to decide between the various alternatives.

The above questions are not unconnected with the phenomenon of fluorescence shown by some of these substances. This aspect will now be discussed.

Fluorescence.—The fluorescence of zinc oxide is well known and the variations found in samples prepared in different ways, well established.[32] Titanium dioxide [17] and lead carbonate are generally considered to be non-fluorescent.

A large number of pure substances were examined under the light from a mercury arc, filtered through thick Chance's cobalt glass (365 and 313 mμ lines only). With the exception of carbon black all showed fluorescence to some degree. Freshly precipitated (and dried) and A.R. zinc oxides showed only a very weak brown fluorescence which changed to a bright yellow when heat treated above 800° C. Titanium dioxide showed only a very weak brown fluorescence.

To test the power of these substances to sensitise fluorescence, strong pastes were made up with pure raw linseed oil. Comparisons were made with the dry powders and with a very thin paste of carbon black in the oil. In this paste the weak white fluorescence of the oil was found to be completely suppressed by the carbon black. A.R. zinc oxide pastes gave a strong yellow fluorescence in contrast with the brown of the dry powder and with the carbon black paste. Titanium dioxide pastes gave only an increased intensity with no real change in colour. These results give independent evidence that these substances can pass on some of their absorbed quanta of energy to the oil-solid interface. Here they are emitted as light of longer wave-lengths. Should there be present molecular configurations capable of reacting, the absorbed quanta may provide the energy of activation.

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[30] See A. L. Hughes, *Rev. Modern Physics*, 1936, 8, 294.

[31] Winther's Theory of photosensitisation (*Z. wiss. Photo.*, 1921, 21, 175) involving emission of "anti-Stokes" radiation, has not been generally accepted.

[32] Largely through the work of Beutel and Kutzelnigg—see Radley and Grant, *Fluorescence Analysis in Ultraviolet Light*, 1935, p. 166, for a summary and references.

Conclusions.—Pfund [10] believed that zinc oxide behaved like carbon black in the ultra-violet (as it was itself unaffected by such light), and recommended its use to protect the oil vehicles in paints from destruction. From the experiments described above, one may conclude that the presence of zinc and titanium oxides constitutes a source of photo-activation of chemical processes such as oxidation of oil vehicles and bleaching of adsorbed dyestuffs. The two oxides cannot, however, be classed together as their action is often specific. Zinc oxide is apparently unable to pass on its absorbed energy to adsorbed linseed oil, whereas titanium dioxide can. The reduction of " chalking " by zinc oxide may be attributed to an inner filter effect.

Summary.

The photosensitising power of zinc and titanium oxides, lithopone, lead carbonate and barium sulphate are discussed in relation to their absorption spectra. More accurate measurements of the absorption spectra, obtained from a study of the reflecting power, are described. Possible mechanisms for the photosensitising process are discussed.

The author is indebted to Mr. W. A. Bayliss for his valuable assistance in the experimental work, to Dr. Peierls for his kindness in discussing the problem, and to Messrs. British Titan Products, Ltd., for samples of Titanium white.

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THE FORMATION OF TACTOIDS IN IRON OXIDE SOLS.

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Received 30*th November*, 1936.

In sols containing non-spherical particles the latter may orientate themselves spontaneously, thus forming double refracting spots. These, which we call "tactoids" have been observed in concentrated sols of V_2O_5 and of benzo-purpurine.[1] In the polarisation microscope between crossed nicols they appear as flame-like spots in the layer of liquid contained between objective and cover-glass. They may be destroyed, for instance, by moving the cover-glass, but are formed again in course of time. Under the ultramiscoscope it was seen that the rod-shaped particles of these sols lie with their long axes practically parallel to the long axis of the tactoids.[2]

In "iron oxide" sols, whose particles are also markedly non-spherical, structures of exactly this type have so far not been observed, but closely related ones, the so-called iridescent layers are found.[3] The plate-like particles of these sols orientate themselves in regular layers on the bottom of the vessel or on the objective, the large plane of the plate lying practically parallel to the wall of the vessel or to the plane of the objective. The regularity of orientation is so great that it causes the beautiful iridescence. This behaviour is quite reversible: they are destroyed by shaking but form again in course of time.

According to X-ray analysis the particles in these iridescent layers are small, but after being shaken up they settle quicker than would be expected from their size.[4] This is probably due to the fact that, after being shaken up, the particles unite to regularly orientated groups, which are presumably simply individual tactoids which were initially formed and are instrumental in producing the iridescent layers. But the layers have been investigated under conditions where these individual tactoids were most likely not readily observed.

In iron oxide sols prepared in a different way by one of us (K. C.), however, we discovered tactoids more akin to those in V_2O_5-sols. The method adopted differed from those mostly used in that the sols were made from very concentrated solutions. If for instance, fused $FeCl_3 . 6H_2O$ was treated with ammonium carbonate as is done when preparing Graham's well-known sol, tactoids were no longer observed in the resulting colloidal

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[1] H. Zocher, *Ztschr. anorg. Chem*, 1925, **147**, 91; H. Zocher and K. Jacobsohn, *Kolloid-Ztschr.*, 1927, **41**, 220; *Kolloidchem. Beih.*, 1929, **28**, 167.

[2] Tactoids consisting of rod-shaped particles seem to be important in biological processes, the spindle formed in mitosis, for instance, appears to be a tactoid (Freundlich, *Protoplasma*, 1927, **2**, 278): under the microscope the spindle is shown to be built up of orientated, rod-shaped particles (Bèlăr, *Naturwiss.*, 1927, **15**, 725; *Arch. Entwicklungsmech.*, 1929, **118**, 359; *Ztschr. f. Zellforsch. u. mikroskop. Anatom.*, 1929, **10**, 73); the spindle may be double refracting (Runnstrom, *Protoplasma*, 1929, **5**, 218 *et seq*, and particularly W. J. Schmidt, *Naturwiss.*, 1936, **24**, 463). It may be mentioned that tactoids of V_2O_5 and benzopurpurine are formed independently in mixed solutions of both, showing that, like in protoplasm, tactoids can be produced in solutions of other colloids (Freundlich, Söllner and Enslin, *Protoplasma*, 1933, **17**, 489).

[3] H. Zocher, *loc. cit.* (1); H. Zocher and W. Heller, *Ztschr. anorg. Chem.*, 1930, **186**, 75; W. Heller, *C.r.* 1935, **201**, 831.

[4] The facts mentioned in this paragraph from unpublished results by W. Heller and O. Kratky.

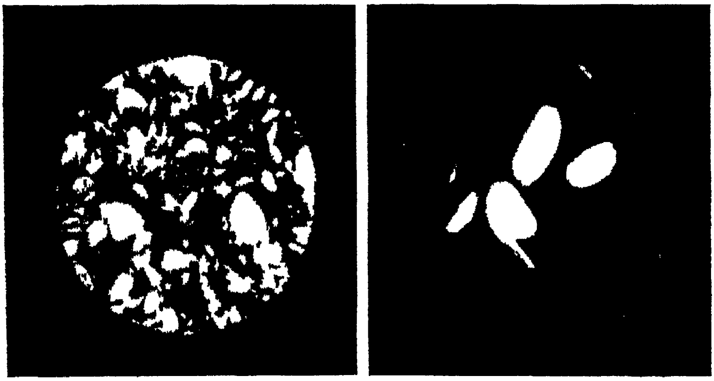

FIG. 1.

[*To face page* 349.

solution when the iron chloride had been dehydrated or the final sol had been heated. A sol made in the following way, however, formed tactoids: iron hydroxide was precipitated from a 30 per cent. solution of iron chloride, kept rather cold, with ammonium hydroxide, the precipitate well washed and separated from the solution by centrifuging; it was then peptised with fused $FeCl_3 . 6H_2O$, 1 c.c. of the latter being mixed with about 15 gm. of the precipitate. The sol was not dialysed; it contained 10 to 15 gm. of iron oxide.

In two to three weeks these colloidal solutions became stream double refracting, and in four to six weeks the tactoids shown in Fig. 1 could be observed under the polarisation microscope between crossed nicols. They are first formed by a small number of particles which still show a marked Brownian movement; this, however, ceases in course of time as the number of orientated particles increases and the packing becomes closer.

These tactoids are superficially rather similar to those in sols of V_2O_5 or benzo-purpurine, but on closer inspection distinct differences are apparent. They are rounded off and do not taper at both ends as is generally the case with the tactoids of the two sols just mentioned. Moreover, the original photographs suggest that they appear serrated at the ends. In V_2O_5 and benzo-purpurine sols the particles of the tactoids always remain in Brownian movement; this is not true for aged tactoids in the iron oxide sol. Furthermore, on moving the cover-glass the tactoids of the latter sol are broken, and not simply dispersed like those of V_2O_5 and benzo-purpurine, suggesting that they are very closely packed and consist of long lamellated particles. This would agree with the results of the investigations on iridescent layers. Both structures appear to be built up of plate-like particles whose large plane is not a square but a rather drawn-out rectangle. So far no X-ray diagram of these tactoids has been determined, but a sol, about 6 months old, from which they were formed was investigated with X-rays by Dr. O. Kratky. Very weak lines of α-FeO(OH) appeared together with an amorphous ring frequently found also in other iron oxide sols, and probably consisting of crystalline plates of α-FeO(OH) which are so thin that they cannot give interference lines.[5] There is no indication of a basic chloride but several points might be brought forward in favour of its presence in the sol. The large amount of chloride, for instance, introduced for peptising the iron hydroxide and the fact that a somewhat narrow range in the proportion of these components is needed for producing sols which form tactoids. The method of preparing the sol is, further, in many respects similar to that used in preparing Graham's sol, and in these, particularly as long as they are young, the presence of a basic chloride has been proved by X-ray analysis.[6] Hence it is probable that in our case also a basic chloride is initially formed, but it may have been transformed rapidly into a hydroxide, a process, which, it is known, will proceed quickly under suitable conditions. The narrow range in the rate Fe-chloride/Fe-hydroxide is also not a decisive argument in favour of a basic chloride, because it may be necessary to guarantee a favourable p_H: iridescent layers are known to form in sols of iron hydroxide only with in a narrow range[7] of p_H, and this is probably also true for these tactoids. Any particles of a basic chloride still present in the fairly old sol used for X-ray measurements must have been too small or too thin to be clearly observed.

The magneto-optical behaviour of this sol was investigated by Dr. W. Heller. The light rays passed normally to the lines of force through the sol. The magnetic double refraction of the latter was weak. But the plane of rotation was turned strongly by the magnetic force. This is not due to true dichroism, because the rotation was observed in a range of the spectrum where the absorption was weak. The marked discrepancy between weak double refraction and strong rotation is also rarely found in dichroism. The strong rotation is obviously due to dityndallism, *i.e.*, to the difference in the indices of the scattering of the ordinary and extraordinary ray. Dityndallism caused by streaming is fairly strong, if the sol is diluted; streaks are observed on stirring. All these facts favour particles which have one long axis, but are very thin.

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[5] W. Heller, O. Kratky and H. Nowotny, *C.r.*, 1936, **202**, 1171.

[6] W. Heller, O. Kratky and H. Nowotny, *loc. cit.* (5).

[7] H. Zocher and W. Heller, *loc. cit.* (3) and unpublished results by W. Heller and O. Kratky, *loc. cit.* (4).

The particles in the tactoids are well orientated; they may disappear almost entirely if their long axis is parallel to one of the directions of polarisation.

The fact that these particular tactoids are found, whereas iridescent layers have so far not been observed in sols of this kind is due probably to their high viscosity. High viscosity naturally opposes settling down as iridescent layers, but favours the observation of individual tactoids in the liquid.

These tactoid-forming sols are strongly thixotropic, setting to a gel in the course of some hours without addition of any further electrolyte and being liquefied again on shaking. The phenomenon was so far fully reversible.

Summary.

In iron oxide sols prepared by peptising precipitated iron hydroxide in water with fused $FeCl_3 . 6H_2O$, the formation of tactoids, *i.e.*, a spontaneous orientation of particles was observed. These tactoids are in some ways similar to those observed in V_2O_5- and benzo-purpurine sols.

We have much pleasure in thanking Dr. W. Heller and Dr. O. Kratky for valuable suggestions and active help.

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A METHOD FOR DETERMINING THE DISTRIBUTION OF MOLECULAR WEIGHTS IN MACROMOLECULAR SUBSTANCES.

BY H. DOSTAL AND H. MARK.

Received 16*th November*, 1936.

Macromolecular substances, whether occurring naturally or prepared artificially, are invariably mixtures of molecules of different dimensions, so long as they have not been fractionated into more or less homogeneous fractions. Different methods are in use for the determination of the *mean* molecular weight of such macromolecular systems; *e.g.*, Staudinger's method based on the measurement of viscosity; and the methods using, directly or indirectly, the estimation of osmotic pressure. When, however, it is sought to determine not only the mean size of the molecules, but also the distribution of the actual molecular dimensions around this mean value, great difficulties are encountered. According to Kraemer and Lansing[1] a determination of the distribution law is possible by means of Svedberg's ultracentrifuge.[2]

We shall now describe another and more readily available method of attacking the problem. It is based on the fact that the mean molecular weights differ as they are determined respectively from the osmotic pressure, or from viscosity, and coincide only in the special case of a completely homogeneous system. In order to prevent misunderstandings we emphasize that we are dealing here with *chain molecules* only, so that a given molecular size is equivalent to a certain number of chain links.

The Mean Molecular Size from Viscosity.

The specific viscosity of a dissolved substance with chain molecules (*i.e.*, the viscosity of the solution less that of the pure solvent) follows Staudinger's rule in the case of sufficiently dilute solutions. According to this rule, the specific viscosity (per unit mass) at a given concentration is proportional to the molecular size, but for any given size it is proportional to the concentration. If the part f_i of the whole mass of the substance is formed by molecules of the chain-length i, the specific viscosity must be proportional to

$$\bar{i} = \sum_{i=1}^{\infty} i f_i. \qquad (1)$$

Since

$$\sum_{i=1}^{\infty} f_i = 1,$$

we can write

$$\bar{i} = \frac{\Sigma i f_i}{\Sigma f_i}. \qquad (2)$$

The mean value $\bar{i}$ can thus be determined from viscosity measurements as soon as the method has been standardised by reference to a different method of estimation.

Considering now, instead of relative masses f_i, the relative numbers of particles:

$$g_i = \frac{f_i}{i} \qquad (3)$$

we obtain from (1)

$$\bar{i} = \Sigma i^2 g_i \qquad (1')$$

We observe that the viscosity due to a particle is proportional to the *square* of its size. As first suggested by H. Mark,[4] this fact is best explained by assuming the same relationship for the mean volume occupied by a chain-molecule, subject to Brownian movement. Analogously, it follows from (2):

$$\bar{i} = \frac{\Sigma i^2 g_i}{\Sigma i g_i}. \qquad (4)$$

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[1] Kraemer and Lansing, *Z. physik. Chem.*, 1935, **39**, 153; *J.A.C.S.*, 1935, **57**, 1369.

[2] R. Signer and H. Gross, *Helv. Chim. Acta*, 1934, **17**, 335, 726.

[3] E. Guth and H. Mark, *Ergebn. exakt. Naturw.*, 1933, **12**, 127; W. H. Carothers *Trans. Faraday Soc.*, 1936, **32**, 47.

[4] H. Mark, Diskussion zu H. Staudinger, *Z. Elektrochemie*, 1934, **40**, 449.

The Mean Molecular Size from Osmotic Pressure.

Another mean value is obtained from measurements of the osmotic pressure, including the cryosopic method. The osmotic pressure is a function of the number of dissolved particles and is thus a function of Σg_i. The mean value of i obtained in this way is:

$$\bar{\bar{i}} = \frac{\Sigma i g_i}{\Sigma g_i} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

since $\Sigma i g_i = \Sigma f_i = 1$.

Now, it is not necessary, in order for (4) and (5) to be valid that g_i, *i.e.*, the relative ordinates of the distribution curve, should be standardised in the same way as in (3); they may quite well differ from f_i/i by an arbitrary constant factor. If molecules of one size only are present, $\bar{i}$ must be equal to $\bar{\bar{i}}$, since otherwise the quotient $r = \bar{\bar{i}}/\bar{i}$ would not be unity. The value of r is obviously related to the relative variations of the molecular sizes. The complex distribution curve cannot, however, be obtained from $\bar{i}$ and $\bar{\bar{i}}$ alone, because two measurements are insufficient to determine a curve.

Combination of the Two Mean Values.

The basis of the measurements can be broadened by separating the complex system into two fractions I and II, determining both values for each fraction. With the new values $\bar{i}_{\mathrm{I}}$, $\bar{\bar{i}}_{\mathrm{I}}$, $\bar{i}_{\mathrm{II}}$, $\bar{\bar{i}}_{\mathrm{II}}$ there are, then, six independent figures. Before these data can be used, however, it is necessary to know the distribution of the size i between the two fractions I and II. Let this distribution be α_i and β_i ($\alpha_i + \beta_i = 1$). Assuming that α_i and β_i are known, we obtain from (4) and (5) the equations

$$\left.\begin{array}{ll} \bar{i}\Sigma i g_i = \Sigma i^2 g_i & \bar{\bar{i}}\Sigma g_i = \Sigma i g_i \\ \bar{i}_{\mathrm{I}}\Sigma i\alpha_i g_i = \Sigma i^2\alpha_i g_i & \bar{\bar{i}}_{\mathrm{I}}\Sigma \alpha_i g_i = \Sigma i\alpha_i g_i \\ \bar{i}_{\mathrm{II}}\Sigma i\beta_i g_i = \Sigma i^2\beta_i g_i & \bar{\bar{i}}_{\mathrm{II}}\Sigma \beta_i g_i = \Sigma i\beta_i g_i \end{array}\right\} . \quad . \quad . \quad (6)$$

There are thus six linear homogeneous equations for the determination of the very numerous unknown quantities g_i. The relative values of these quantities, and thus the relative ordinates of the distribution curve, could be calculated if their number could be reduced to 7, because 7 quantities give 6 relations. The required reduction in the number of variables can be attained by dividing the whole field of possible molecular sizes i into 7 intervals, all particles belonging to one of these intervals forming a group g_i.

The boundaries of the intervals $i_0 = 1$, i_1, i_2, i_3, i_4, i_5, i_6, i_7 must be chosen in such a way that the possibility of $i > i_7$ is practically excluded. Writing:

$$G_a = \sum_{i=i_a}^{i_{a+1}-1} g_i \quad . \quad . \quad . \quad . \quad . \quad (7)$$

we obtain, approximately,

$$\sum_{i=i_a}^{i_{a+1}-1} i g_i = i_{a+\frac{1}{2}} G_a . \quad . \quad . \quad . \quad . \quad (7')$$

and
$$\sum_{\imath=i_a}^{i_{a+1}-1} i^2 g_i = i^2_{a+\frac{1}{2}} G_a \quad . \quad . \quad . \quad . \qquad (7'')$$

where the indices $i_{a+\frac{1}{2}}$ refer to some appropriate points near the middle of the intervals in question. It is assumed that the curve changes more or less smoothly within the limits of a single interval. From (7), (7′) and (7″) we may write instead of (6)

$$\left.\begin{array}{ll} \sum\limits_0^6 i_{a+\frac{1}{2}}(i_{a+\frac{1}{2}} - \bar{\imath})G_a = 0 & \Sigma(i_{a+\frac{1}{2}} - \bar{\bar{\imath}})G_a = 0 \\ \Sigma i_{a+\frac{1}{2}}(i_{a+\frac{1}{2}} - \bar{\imath}_{\mathrm{I}})\bar{\alpha}_a G_a = 0 & \Sigma(i_{a+\frac{1}{2}} - \bar{\bar{\imath}}_{\mathrm{I}})\bar{\alpha}_a G_a = 0 \\ \Sigma i_{a+\frac{1}{2}}(i_{a+\frac{1}{2}} - \bar{\imath}_{\mathrm{II}})\bar{\beta}_a G_a = 0 & \Sigma(i_{a+\frac{1}{2}} - \bar{\bar{\imath}}_{\mathrm{II}})\bar{\beta}_a G_a = 0 \end{array}\right\} \quad . \qquad (6')$$

The $\bar{\alpha}_a$*'s* and $\bar{\beta}_a$*'s* are appropriate mean values of $\alpha_\imath$*'s* and $\beta_\imath$*'s*. The calculation of the 6 relationships of the 7 variables G_0, G_1 . . . G_6 from (6′) is a matter of linear algebra, and is easily carried out if the values of $\alpha_\imath$ and $\beta_\imath$ needed for the calculation of $\bar{\alpha}_a$ and $\bar{\beta}_a$ are known. Two methods are available for the experimental determination of the distribution coefficients α_i and $\beta_\imath$.

1. A small quantity of as homogeneous as possible a fraction is prepared, its molecular size is determined and it is " labelled " by substituting in it some element which can easily be determined analytically, *e.g.*, iodine. This sample is then added to the mixture investigated and the fractionating process carried out as usual. The determination of iodine in the two fractions I and II would then suffice to give the values α_i and $\beta_\imath$ for a certain value of i, corresponding to the molecular size of the indicator fraction. Further points of the α_i and β_i curves can be obtained by using homogenised sample with a lower molecular weight: the determination of the rest of the curves by linear interpolation will probably not involve any serious errors.

2. An inhomogeneous mixture of known composition is obtained from artificially prepared homogeneous fractions, which are admixed to give the six mean values $\bar{\imath}$, $\bar{\bar{\imath}}$, $\bar{\imath}_{\mathrm{I}}$, $\bar{\bar{\imath}}_{\mathrm{II}}$ . . . so that the experimental conditions for the separation into the fractions I and II are established. The equations (6′) can now be used for the determination of $\bar{\alpha}_a$ and $\bar{\beta}_a$, since G_a is now known. The two first equations (6′) do not, however, contain the distribution coefficients so that we now have only 4 equations for 7 unknown quantities (the β_i*'s* do not count separately), *i.e.*, we are short of 3 equations. If, however, we make the additional assumption that the distribution coefficient changes linearly in the 5 middle intervals of the 7, a solution can be obtained.

The above described method for the calculation of a distribution curve for the molecular weights of a polymeric substance which cannot be found by fractionation appears to us to be the only one permitting direct investigation of the degree of heterogeneity of a high-polymer substance without the use of the ultracentrifuge, *i.e.*, with the means available in an ordinary physico-chemical laboratory.

We shall shortly publish some results showing the experimental application of this method both to mixtures of long chain paraffins and to high polymeric substances.

Wien, I. Chemisches Universitäts-laboratorium.

REVIEWS OF BOOKS.

Properties of Matter. By F. C. Champion and N. Davy. Blackie & Sons, London, 1936. Pp. xiv + 296. Price 15s.

This treatise may be very heartily commended to the student of final and honours grade in the Universities. It is detailed enough to give the reader thoroughly interesting accounts of the most recent work on the topics of which it treats, and it is not overburdened with unessential matter.

The authors have been able to give attention to detail, and at the same time to keep the book down to manageable dimensions by a careful choice of subject, the main headings of the contents being Units and Dimensions, *g* and *G*, Elasticity, Compressibility, Seismic waves, Capillarity, Surface Films, Kinetic Theory, Osmotic Pressure, Diffusion, Viscosity and the determination of Planck's Constant. References are given to papers of outstanding interest and importance, and sets of examples are supplied on which the student may test his skill.

A student of first year honours grade who has worked critically through the book will find himself very well equipped for a systematic study of the original literature in any of these copies to which he may desire to give special attention.

The book is well produced and fills a gap in the literature of physics.

A. F.

Textbook of Quantitative Inorganic Analysis. By I. M. Kolthoff and E. B. Sandell. Pp. xv + 749. New York: The Macmillan Co., 1936. Price 20s. net.

The name of Professor Kolthoff as author is sufficient to justify the expectation that a book bearing it will be of high standard. The present volume is in every way worthy of his reputation. It is divided into parts dealing with gravimetric analysis, volumetric analysis, physico-chemical methods (colorimetry and spectroscopy; short accounts of various physico-chemical methods with references to literature), analyses of complex materials (brass, steel, silicate rocks) and appendices of tables. Great stress is laid on the theoretical aspects of the subject: the old theory of solubility product, which still finds a place in most books, is drastically modified in the light of modern research on activity, co-precipitation, etc., and the theory of p_H and indicators is also on very modern lines. The result is that the divorce between theory and practice, which most teachers and students felt in the older presentation, has now disappeared. These sections are usually much better presented than in books on physical chemistry, so that the student will find them sufficiently detailed to be of real value and will see the relation to the practical details which are also given. The descriptions of the analytical procedure are full, so that there is every reason to expect that satisfactory results will be obtained. From the point of view of the courses given in English universities the book will need supplementing, since the gravimetric determinations do not include some elements commonly dealt with.

J. R. P.

ABERDEEN: THE UNIVERSITY PRESS

ERRATA.

Pages 147 and 148. In Figs 1 and 2, *for* Stannic chloride *read* Silicon chloride.

Page 163. In the last line of the second group of formulæ, *for* $V\alpha_0{}^M\ \beta_0$, etc., *read* $V^M\alpha_0/\beta_0$, etc.

Page 244. First long paragraph, 7th line, *after* "molecules" *add by footnote*, "See page 267 for a correction of fact, but not of argument"

Page 251. After the two formulæ between those numbered respectively (7) and (10) *add* the respective numbers (8) and (9).

Page 252. Fifth line, *for* "article 1*b*" *read* "article 1(*b*)."

ACID—BASE CATALYSIS IN GAS REACTIONS. PART I. THE DEPOLYMERISATION OF PARALDEHYDE.

By R. P. Bell and R. le G. Burnett.

Received 7th December, 1936.

Introduction.

Kinetic measurements on reactions catalysed by acids or bases have so far been almost entirely confined to reactions in solution, and it is the purpose of the present series of papers to investigate how far reactions of this type can take place in the absence of a solvent. Several cases are known in which acids or bases exert a catalytic effect in inert solvents of the hydrocarbon type,[1] and it might be anticipated that a similar state of affairs would obtain in analogous gas reactions. A study of such gas reactions would provide useful information about the effect of the solvent on the tendency of molecules to gain or lose protons.

The conversion of paraldehyde to acetaldehyde in inert solvents has been shown [2] to be a unimolecular reaction exhibiting general acid catalysis. In the gas phase the spontaneous change has been studied by Coffin [3] who found it to be a homogeneous unimolecular decomposition taking place at a measurable rate above about 210° C. It should therefore be possible to investigate acid catalysis in the gas reaction between 100° and 200° C.

Materials.

Coffin found that small traces of oxygen had a considerable retarding effect on the spontaneous decomposition, and precautions were therefore taken to exclude air from the materials used. A pure specimen of *paraldehyde* was dried over sodium and distilled in a current of nitrogen, the fraction 121°-123° being collected. It was then distilled *in vacuo* directly into a bulb on the apparatus. After sealing off, the paraldehyde in the bulb was frozen and any gas pumped off. *Hydrogen bromide* was prepared in a previously evacuated all-glass apparatus by the action of bromine on red phosphorus and water. Free bromine was removed by moist red phosphorus and moisture by phosphorus pentoxide. *Hydrogen chloride* was similarly prepared from sulphuric acid and sodium chloride, and dried with phosphorus pentoxide.

Experimental Method.

The reaction was followed by measuring the pressure change at constant volume by means of a mercury manometer. The apparatus is shown schematically in Fig. 1. The reaction vessels were about 100 c.c. in capacity and were heated in vapour jackets (water 100°, tetrachloroethane 143°, pentachloroethane 154°, decalin 190°). All tubes and taps in communication with the bulb were kept at about 80° by a winding of nichrome wire. The small catalyst pressures required were obtained by using the subsidiary manometer A, in which the right hand mercury surface was brought to the mark B and the pressure read off at C. The sharing factor between A and the reaction vessel was about 1 : 20. The catalyst was admitted to the reaction vessel first. A mercury vapour pump was used for evacuation.

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[1] See *e.g.*, R. P. Bell, *Proc. Roy. Soc.*, *A*, 1934, 143, 377.

[2] R. P. Bell, O. M. Lidwell and M. W. Vaughan-Jackson, *J. Chem. Soc.*, 1936, 1792.

[3] *Canad. J. Research*, 1932, 7, 75.

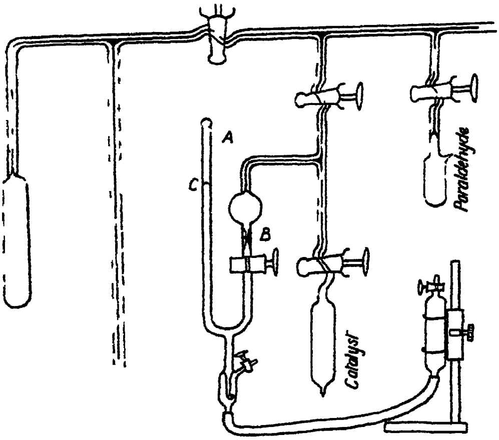

Fig. 1.

Reaction Products.

In experiments of intermediate velocity it was possible to determine the final reading directly and the initial reading by a small extrapolation, and hence to find the proportional pressure increase (p_∞/p_0). Table I. shows some results obtained in this way.

These results agree well with the assumption that the paraldehyde is quantitatively converted to acetaldehyde, which would result in a three-fold pressure increase. As a further test, the acetaldehyde formed was determined chemically in separate experiments. A thin bulb containing 0·01-0·03 g. of paraldehyde was enclosed in a sealed tube of soft glass containing hydrogen bromide or chloride at a pressure of a few centimetres. The tube was heated to about 100° C. and the bulb broken by shaking. The temperature was maintained at 100° for a short time, after which the tube was rapidly cooled and the tip broken off under a strong solution of potassium bisulphite. The acetaldehyde formed was determined by the method of Friedman, Cotonio and Shaffer,[4] titration being carried out with $N/20$ iodine solution. The results are given in Table II.

TABLE I.

p_0 (mm.).	Catalyst.	p_∞/p_0.
68·7	0·802 mm. HBr	2·85
39·4	0·851 " "	2·85
61·3	0·591 " "	2·97
79·5	0·405 " "	3·03
74·0	0·239 " "	3·00
63·4	8·87 mm. HCl	2·99
62·4	4·45 " "	3·02
	Mean =	2·97

These results agree fairly well with the pressure increase, though on the whole they indicate a slightly less complete conversion. This may possibly be due to a partial reversal of the equilibrium on cooling the tubes, or to some irreversible polymerisation on the surface of the tubes, which had not been "aged" before use (*cf.* next section). It is at least safe to say that more than 95 per cent. of the paraldehyde is converted to acetaldehyde under the conditions of our experiments.

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[4] *J. Biol. Chem.*, 1927, **73**, 342.

TABLE II.

Catalyst.	Paraldehyde Taken.	Acetaldehyde Found.	Difference.
HCl . .	0·0134 g	0·0131 g.	— 2 per cent.
HCl . .	0·0208 g	0·0202 g.	— 3 ,,
HCl . .	0·0226 g	0·0218 g.	— 4 ,,
HBr . .	0·0071 g.	0·0069 g.	— 3 ,,
HBr . .	0·0134 g	0·0137 g.	— 2 ,,
HBr . .	0·0274 g.	0·0268 g.	— 2 ,,

General Characteristics of the Reaction Kinetics.

As would be expected from Coffin's results, the rate of reaction in the absence of catalyst was negligible at the temperatures used in this investigation. Small quantities of hydrogen bromide or chloride were however found to cause a rapid reaction. When a fresh bulb was used, the reactions were very fast and unreproducible, and in each experiment the rate decreased much more rapidly than it should do in a unimolecular reaction. However, if successive reactions were carried out in the same vessel, the velocity (for a given catalyst concentration) decreased steadily and the reactions deviated less and less from a unimolecular course. Finally a state was reached in which the rates were fairly reproducible and the course of the reactions unimolecular. If the bulb was now baked out at about 700° C. the rates again became rapid and unreproducible. A steady rate could be obtained once more by carrying out more experiments in the bulb, but this rate usually differed somewhat from the value obtained (with the same catalyst concentration) before baking out. The same general behaviour was observed in vessels of soda glass, pyrex and silica, and the final steady rates were not markedly different in the three types of vessel. Experiments in which small quantities of air were admitted (see Table IV.) showed that none of the irregularities observed were due to traces of air, as in Coffin's work on the spontaneous reaction.

This behaviour strongly suggests that the catalysed depolymerisation takes place on the surface of the vessel, which is gradually poisoned as successive reactions are carried out. It was found that the process of " aging " was greatly accelerated by allowing the products of the reaction to remain for some hours in the reaction vessel, when a slight decrease of pressure often took place. The poisoning may thus well be due to the deposition of a highly polymerised form of acetaldehyde, volatilised (or decomposed) only at a high temperature. Experiments with packed bulbs indicate that the reaction is largely heterogeneous even in " aged " bulbs, since the final steady rate is always increased by packing (see Tables IV. and V.). On account of the unreproducible nature of the surface, a direct proportionality between the surface-volume ratio and the reaction velocity is hardly to be expected. The process of aging was much slower in packed bulbs. Measurements were attempted in a pyrex vessel in which the surface-volume ratio had been increased by a factor of 75 by packing, but it was not found possible to obtain any unimolecular or reproducible experiments. Determinations of the temperature coefficient (*v. infra*) also lend strong support to the view that the velocities measured are essentially those of a heterogeneous reaction.

Calculation of Velocity Constants.

The unimolecular velocity constants were calculated by plotting $\log_{10}(p_\infty - p)$ against the time, and measuring the slope of the line obtained. For fast reactions p_∞ was observed directly, while for slow reactions it was calculated from the observed initial pressure and the theoretical total pressure change. Reactions in "aged" bulbs always gave straight lines (with the exception of the first few readings). The unimolecular course of the reaction is illustrated by Table III., which gives details of a typical experiment, and velocity constants calculated for each reading by the equation

$$-kt = \log_{10}\frac{p_x - p}{p_\infty - p_0}$$

It will be seen that the reaction is strictly unimolecular over more than 90 per cent. of its course.

TABLE III.*

	Secs.	$p_x - p$.	k.	Mins.	Secs.	$p_x - p$.	
0	0	(149·2)	—	2	10	35·0	0·291
0	10	131·2	(0·371)	2	20	29·0	0·306
0	20	118·0	0·306	2	30	25·8	0·305
0	30	105·2	0·304	2	40	22·8	0·306
0	40	94·5	0·299	2	50	20·3	0·306
0	50	82·0	0·312	3	00	18·0	0·306
1	00	73·1	0·310	3	10	16·0	0·306
1	10	66·0	0·304	3	20	14·2	0·307
1	20	57·8	0·310	3	30	12·2	0·311
1	30	52·2	0·305	3	40	11·3	0·305
1	40	46·3	0·304	3	50	10·3	0·303
1	50	42·2	0·300	4	00	9·2	0·302
2	00	39·0	0·292	—	—	—	—
						Mean k =	0·304
					k from logarithm plot =		0·306

* Unpacked silica bulb, 100° C. Initial pressure of paraldehyde (extrapolated) = 74·6 mm. Pressure of HBr in subsidiary manometer = 41·8 mm. Pressure of HBr in reaction vessel = 1·69 mm. p_∞ measured after thirty minutes.

Results.

In the following tables all pressures are expressed in millimetres, and velocity constants in terms of minutes and decadic logarithms. In the case of experiments at temperatures other than 100° the recorded partial pressure of catalyst is obtained by multiplying the actual pressure by the factor $(273 + t)/373$, thus facilitating comparison between equal volume concentrations of catalyst at different temperatures. The experiments within each bracket were carried out in the same reaction vessel without any intermediate treatment, and are therefore comparable.

Order of the Reaction.

As stated above, the course of single experiments indicates that the reaction is unimolecular with respect to paraldehyde (*cf.* Table III). The effect of varying the initial pressure of paraldehyde or catalyst can only be derived from sets of experiments under comparable surface conditions (bracketed in the above tables). The paraldehyde pressure has not been varied very widely, but over the range investigated there is no effect greater than the fluctuations due to variability of surface (see particularly series (*e*) and (*l*)), thus confirming the view that the reaction is of the first order with respect to paraldehyde.

TABLE IV.

	p (Paraldehyde).	p (HBr).	$10^3 k$.	$10^3 k/p$ (HBr).
Catalysis by Hydrogen Bromide in Unpacked Bulbs.				
100° C.				
(*a*) Silica . .	60·7	0·316	57·4	182
	62·3	0·410	48·4	118
	65·7	0·895	211	237
	68·3	1·28	205	160
	74·6	1·69	306	181
	57·4	2·61	508	194
				Mean = 179
(*b*) Silica . .	61·3	0·591	8·5	14·3
	68·1	2·48	100	41·2
	64·4	2·93	81·0	27·6
	71·1	3·78	121	32·0
	60·5	4·39	94·6	21·6
	69·5	5·21	142	27·3
	70·0	6·58	206	31·2
				Mean = 24·4
(*c*) Silica .	82·5	3·22	39·0	12·1
	§70·8	4·17	44·1	10·6
	62·5	6·26	56·4	9·0
				Mean = 10·6
(*d*) Pyrex .	74·7	0·507	62·6	123
	*79·1	0·549	44·5	81
	65·9	0·849	107	126
	*72·1	0·926	215	232
	50·0	1·02	182	178
	*67·7	1·04	215	207
	52·8	1·50	307	204
	60·6	1·95	348	178
				Mean = 169
(*e*) Pyrex .	79·5	0·405	52·8	116
	75·7	0·590	86·6	147
	69·4	0·677	185	272
	73·4	0·730	106	145
	45·0	0·862	152	176
	†74·5	0·960	163	164
	64·8	1·05	235	224
	55·0	1·11	181	163
	21·3	1·14	310	272
	117·7	1·14	201	171
	81·4	1·25	221	177
	65·4	1·40	260	186
	89·0	1·65	310	188
				Mean = 184

* 0·2 — 0·5 mm. air present.

§ Done after series (*g*) at 144°.

† Done after series (*f*) at 144°.

TABLE IV (*continued*).

	p (Paraldehyde).	p (HBr).	$10^3\,k$.	$10^3\,k/p$ (HBr).
144° C.				
(f) Pyrex . .	70·8	1·07	35·2	32·6
	74·0	2·39	86·0	36·2
	63·1	3·28	129	39·2
	72·4	4·74	108	22·8
	80·3	5·82	157	27·0
	71·7	7·56	279	36·8
				Mean = 32·4
(g) Silica . .	70·0	3·49	26·0	7·45
	49·8	4·77	25·6	5·37
	74·7	5·73	23·8	5·00
				Mean = 5·94
190° C.				
(h) Silica . .	40·7	7·40	12·6	1·70
	46·2	9·21	12·0	1·30
	33·0	11·25	23·9	2·12
	49·6	11·30	17·6	1·56
	45·5	15·5	24·6	1·59
				Mean = 1·65

Catalysis by Hydrogen Bromide in Packed Bulbs.

	p (Paraldehyde).	p (HBr).	$10^3\,k$.	$10^3\,k/p$ (HBr).
100° C.				
(i) Pyrex: Surface increased 5 : 1 by packing	63·5	0·502	202	403
	74·0	0·690	214	310
	47·4	0·913	605	650
	63·2	0·933	583	625
	71·2	1·24	566	457
				Mean = 489

The pressures of hydrogen bromide and hydrogen chloride have been varied over a range of 1 : 10 and 1 : 60 respectively, and in each case the velocity is proportional to the first power of the catalyst concentration, as is shown by the absence of any trend in the values of the catalytic constant given in the last column of Tables IV. and V. (This proportionality also confirms the view that the effect of the acids is truly catalytic). It is interesting to contrast this result with the behaviour of the same reaction catalysed by hydrogen chloride in anisole solution, where it was found [5] that the velocity is proportional to the *second* power of the catalyst concentration. In order to interpret the results for catalysis by other acids in solution, it was found necessary to assume a composite mechanism involving first, second and third order reactions with respect to the acid, the first order reaction being most prominent with the strongest acids and in solvents with no basic properties. The change in order from two to one in passing from anisole solution to the vapour may represent an extreme case of this solvent effect.

[5] R. P. Bell, O. M. Lidwell and M. W. Vaughan-Jackson, *J. Chem. Soc.*, 1936, 1792.

TABLE V.

	p (Paraldehyde).	p(HCl).	10^3k.	$10^3k/p$(HCl).
Catalysis by Hydrogen Chloride in Unpacked Bulbs.				
100° C.				
(*j*) Soda glass .	57·0	1·63	6·9	4·22
	60·9	2·91	14·3	4·42
	56·9	3·64	16·4	4·52
	51·6	5·47	26·8	4·23
	62·7	6·40	26·8	4·19
			Mean =	4·32
(*k*) Pyrex .	55·1	1·10	2·24	2·04
	56·3	1·74	4·08	2·44
	50·7	2·48	5·85	2·38
	46·6	2·58	8·50	3·30
	57·9	3·89	8·80	2·26
	55·1	5·52	11·4	2·07
	49·3	6·44	16·5	2·19
	51·5	7·90	17·9	2·26
	58·2	10·27	12·3	1·20
	38·3	15·1	24·0	1·61
	46·8	20·1	20·3	1·01
	39·0	28·2	39·2	1·39
	34·6	60·6	90·0	1·49
			Mean =	1·96
(*l*) Silica . .	27·5	3·49	2·05	0·587
	30·6	3·49	1·28	0·367
	41·8	3·49	1·62	0·463
	50·5	3·54	1·00	0·282
	52·2	3·46	0·96	0·277
	85·3	3·45	1·60	0·465
	88·7	3·56	3·40	0·851
			Mean =	0·470
154° C.				
(*m*) Silica .	67·1	3·25	4·66	1·63
	90·4	5·44	6·00	1·25
	43·5	6·05	10·8	2·04
	90·5	6·05	7·75	1·28
	66·7	6·16	7·62	1·41
			Mean =	1·52
Catalysis by Hydrogen Chloride in Packed Bulbs.				
100° C.				
(*n*) Pyrex: Surface increased 3·3 : 1 by packing	74·3	2·75	6·25	2·27
	62·4	4·45	7·90	1·77
	59·1	5·06	11·3	2·23
	46·3	5·12	16·5	3·23
	55·7	8·43	24·4	2·80
	51·4	8·75	38·8	4·43
	63·4	8·87	21·3	2·40
	61·1	11·52	21·3	1·86
	59·0	13·80	23·1	1·67
			Mean =	2·52

Temperature Coefficient.

The only reliable data on the temperature coefficient are those for hydrogen bromide at 100° and 144° (series (*c*), (*e*), (*f*) and (*g*)). The mean value of the catalytic constant for twelve experiments in a pyrex bulb was 18·4. On raising the temperature to 144° the mean value for six experiments was 32·4, while on returning to 100° a value of 16·4 was obtained, showing that the state of the surface was not materially altered by the change of temperature. Similar experiments with a silica bulb gave 10·6 at 100°, 5·94 at 144°, and 10·6 again on returning to 100°. Some experiments in silica at 190° (series (*h*)) show a further decrease in catalytic constant to 1·65, but these were carried out in a different reaction vessel, and are therefore not strictly comparable. It is however clear that the temperature coefficient is negative and varies in different vessels: this provides very strong evidence that the reaction is predominantly heterogeneous. The data for hydrogen chloride in silica at 100° and 154° (series (*l*) and (*m*)) indicate a small positive temperature coefficient for this catalyst, but in this case there was no check on the constancy of the surface conditions by returning to the lower temperature.

Catalysis by Other Acids.

Pressures of about 1 mm. of *hydrogen iodide* in a silica bulb at 100° caused reactions too fast to measure. Partly on this account, and partly because small quantities of iodine present fouled the mercury, no quantitative measurements were attempted. It is, however, clear that this acid is much more active than hydrogen chloride or bromide, as would be expected from the order of acid strengths. Using the weak acid, *acetic acid*, no catalysis could be detected with 30 mm. of catalyst at 100° or 154°. The somewhat stronger *formic acid* gave a very slow reaction with 12 mm. at 144°. *Dichloracetic acid* was difficult to study on account of its low volatility, but it was found that pressures of about 1 mm. at 190° gave reactions which were perceptibly faster than the spontaneous reaction. *Sulphur dioxide* has been reported to be a catalyst for the reaction in the liquid phase. In the present work the carefully dried gas was without effect at 100°, but the presence of small quantities of moisture rendered it catalytically active. It is possible that this behaviour is due to the formation of molecules of the strong acid H_2SO_3 in the vapour or on the surface.

No quantitative study was attempted with any of the acids mentioned in this section. The reactions involved are almost certainly heterogeneous (as with hydrogen bromide and chloride), and no true comparison of catalytic powers is possible in the absence of adsorption data. The qualitative observations recorded do however establish that in this reaction general catalysis by acid molecules takes place in the absence of a solvent. If a homogeneous gas reaction of this type were discovered the results would be of great interest, and work is continuing along these lines.

Summary.

1. The depolymerisation of paraldehyde vapour is catalysed by hydrogen chloride and hydrogen bromide at temperatures between 100° and 190°. At least 95 per cent. of the paraldehyde is converted to acetaldehyde. The reaction is predominantly heterogeneous, and only takes place at a reproducible rate after the surface of the reaction vessel has become "aged" by contact with the reaction products.

2. The course of each experiment is unimolecular and the velocity constants are independent of the paraldehyde pressure and directly proportional to the catalyst pressure.
3. The temperature coefficient of reaction velocity is negative for catalysis by hydrogen bromide, but appears to have a small positive value with hydrogen chloride.
4. The reaction is also catalysed by hydrogen iodide, formic acid and dichloroacetic acid. Sulphur dioxide is without action when dry, but catalyses in the presence of water vapour. There is no detectable catalysis by acetic acid.

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THE ULTRA-VIOLET ABSORPTION SPECTRA OF IODOFORM AND OF OTHER TRI-IODIDES IN SOLUTION.

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Received 11th December, 1936.

The apparent similarity of the absorption spectra of iodoform and of potassium tri-iodide was first noted by Crymble, Stewart and Wright in 1910.[1] Later quantitative measurements of the absorption spectra were made by Lowry and Sass.[2] According to them, both iodoform and potassium tri-iodide give two bands with maxima at about 2900 and 3500 Å., and the shape of the whole absorption curve is very similar in the two cases. In a further paper on this subject, Gilbert, Goldstein and Lowry,[3] showed that the absorption spectrum of potassium tri-iodide is really characteristic of the I_3^- ion, since the position of the two bands is independent of the cation present in the solution (K^+, Cs^+ or quaternary ammonium ion). Dissociation into $I_2 + I^-$, which is especially marked in aqueous solution, diminishes the intensity of the two bands but does not change the form of the absorption curves, as neither of the dissociation products has any appreciable absorption in the region in which the I_3^- ion absorbs strongly.

Lowry and Sass considered that the similarity in the absorption spectra of iodoform and of the I_3^- ion amounted almost to an identity of the two curves, and that therefore some definite similarity of structure between the two compounds was indicated. Since the ordinary formulæ do not point to any similarity in structure, they suggested that the reason might be found in the presence in both compounds of three contiguous atoms of iodine in the space model " from which all traces of the bonds between the atoms have been erased." This picture is admittedly unconventional, and no definite structural formulæ were put forward. The available evidence on the spatial arrangements of the iodine atoms in the two compounds is opposed to any real similarity of structure. Whereas in iodoform the three iodine atoms form a pyramidal structure with the carbon atom to which they are directly linked, it appears from X-ray measurements that in the I_3^- ion there is, in the crystalline state at any rate, a very nearly linear arrangement of the tri-iodide group.[4] In this complex group two iodine atoms are probably co-ordinated with the third central atom, which has two of its valency group of ten electrons present as an " inert pair." [5]

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[1] Crymble, Stewart and Wright, *Ber.*, 1910, **43**, 1183.
[2] Lowry and Sass, *J.C.S.*, 1926, 622.
[3] Gilbert, Goldstein and Lowry, *J.C.S.*, 1931, 1092.

The experimental observation, therefore, that iodoform and the I_3^- ion give very similar absorption spectra in solution, is not easy to explain theoretically, and it seemed more probable that the absorption curve of iodoform found by Lowry and Sass is not really characteristic of that molecule, but is complicated by the occurrence of reactions in the solution which form I_3^- or HI_3. It is well known [6,7] that solutions of iodoform in alcohol are readily decomposed photochemically with the production of I_2, and in alcoholic solution this would inevitably [8] produce I_3^- or HI_3. Furthermore, Scheibe [9] measured the absorption of iodoform in alcohol and obtained results differing somewhat from those of Lowry and Sass. He also found that the absorption curve in hexane differed slightly from that in alcohol.

It seemed worth while to investigate further the absorption spectrum of iodoform to see to what extent the two so-called iodoform absorption bands are (*a*) really characteristic of the iodoform molecule, and (*b*) occur also in the absorption spectra of other normal tri-iodide molecules of the iodoform type, *i.e.* in which three iodine atoms are covalently linked to some central atom.

For this purpose, measurements of the absorption spectrum of iodoform in alcohol and in cyclohexane have been made, and also of methyl iodoform, for which no previous absorption data exist. The absorption spectra of phosphorus, arsenic and antimony tri-iodides have also been measured. These substances, when dissolved in non-ionising solvents, are largely in the covalent state, there being a gradual increase in the dipole moment of the molecule in passing from phosphorus tri-iodide ($\mu = 0$) to antimony tri-iodide ($\mu = 1{\cdot}58$).[10] Practically no data were available on the absorption of these substances, but since the commencement of this work a paper appeared by Kato and Someno [11] on the absorption spectra of the tri-halides of the phosphorus family in the vapour state and dissolved in ether. These results, which are of a semi-quantitative nature, will be referred to later.

Experimental.

Absorption Measurements.

These were made by using a Hilger rotating sector photometer in conjunction with a tungsten-steel spark as light source and a Hilger medium quartz spectrograph, the spectra being recorded on Wellington Ortho Process plates. The solvents and solutions were contained in 1 cm. quartz cells. In the curves, values of log ϵ are plotted against the corresponding wave-length in A units. The molecular extinction coefficient ϵ is defined by the expression $\epsilon = \frac{1}{cd} \cdot \log \frac{I_0}{I}$, where c is the concentration of the solute in gm. mols./litre, d the length of the absorption cell in cm., and I_0 and I the intensities of the incident and transmitted light, respectively.

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[4] Mooney, *Z. Krist.*, 1935, **90**, 143.
[5] Sidgwick, *Ann. Reports*, 1933, **30**, 126.
[6] Dubrisay and Emschwiller, *Bull. Soc. Chim.*, 1935, **2**, 127.
[7] Gibson and Iredale, *Trans. Faraday Soc.*, 1936, **32**, 571.
[8] Batley, *ibid.*, 1928, **24**, 438.
[9] Scheibe, *Ber.*, 1925, **58**, 586.
[10] Malone and Ferguson, *J. Chem. Physics*, 1934, **2**, 99.
[11] Kato and Someno, *Inst. Phys. Chem. Res. Tokio*, 1935, **28**, 95.

Solvents.

Ethyl alcohol : Absolute alcohol was dried over CaO and redistilled.

Cyclohexane : The "specially purified for spectroscopy" B D.H. Product.

Benzene : A.R. benzene, redistilled.

Preparation of Iodides.

Iodoform : B.D.H. product recrystallised from absolute alcohol, m.p. 118·5° — 119·5° C.

Methyl iodoform : Prepared according to the method given by Boissieu.[12] The preparation was found to be more successful by diluting the methyl chloroform with CS_2 and adding it very slowly to the aluminium iodide solution. The final product was recrystallised from absolute alcohol, and the whole preparation was carried out in the dark. Yellow crystals m.p. 93° C.

Phosphorus tri-iodide : The preparation given by Traxler[7] and Germann,[13] involving the direct combination of the elements in carbon disulphide solution was used. The solvent was removed in a current of dry CO_2, by warming on a water bath. M.p. 57°-61° C.

Arsenic and Antimony tri-iodides : The purest B.D.H. products were recrystallised from "analar" benzene, m.p. 146° C. and 168° C. respectively.

Absorption Spectrum of Iodoform and Methyl Iodoform.

(a) Iodoform in Ethyl Alcohol.—Preliminary measurements, in which the solutions were examined soon after being prepared, but were not protected from exposure to light during the preparation, gave an absorption curve (*cf.* curve 2, Fig. 1) in which the height and position of the two maxima agree fairly well with those of Lowry and Sass.[2] The following experiments show, however, that in such solutions an appreciable amount of photo-decomposition of the iodoform has occurred. Iodoform, which had been recrystallised four times from alcohol, was dissolved in alcohol to a known concentration, the crystallisation and preparation of the solution being performed in the dark. Absorption measurements were then made in which the solution was exposed only to the light of the spark source and, in order to reduce to a minimum the photo-decomposition during this operation, the solution in the cell was renewed after every minute of total exposure to the spark. The absorption curve obtained in this way is shown in curve 1, Fig. 1, and the values of λ_{max} and log ϵ_{max} are tabulated in Table I. The results agree very well with those of Scheibe,[6] who also took precautions to reduce the photo-decomposition of the iodoform during the absorption measurements. The effect of a small amount of decomposition of the iodoform on the absorption curve is illustrated by curves 3 and 4 in Fig. 1. These were obtained with the same solution that gave curve 1, but which had been exposed to ordinary daylight for five and ten minutes respectively, before carrying out the absorption measurements. The result of even these short exposures is that the absorption maxima increase in intensity and at the same time approach the wave-lengths of 2900 and 3600 A., which are the values of λ_{max} characteristic of the two I_3^- bands (*cf.* Table I.). Since the latter are about 15-20 times more intense than the iodoform bands, the height of the absorption curve of iodoform may be appreciably increased by even a small amount of decomposition, and this appears to have occurred under the conditions used by Lowry and Sass, since their absorption curve lies between curves 3 and 4 of Fig. 1.

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[12] Boissieu, *Bull. Soc. Chim.*, 1888 (2), **49**, 16.

[13] Traxler and Germann, *J. Amer. Chem. Soc.*, 1927, **49**, 307.

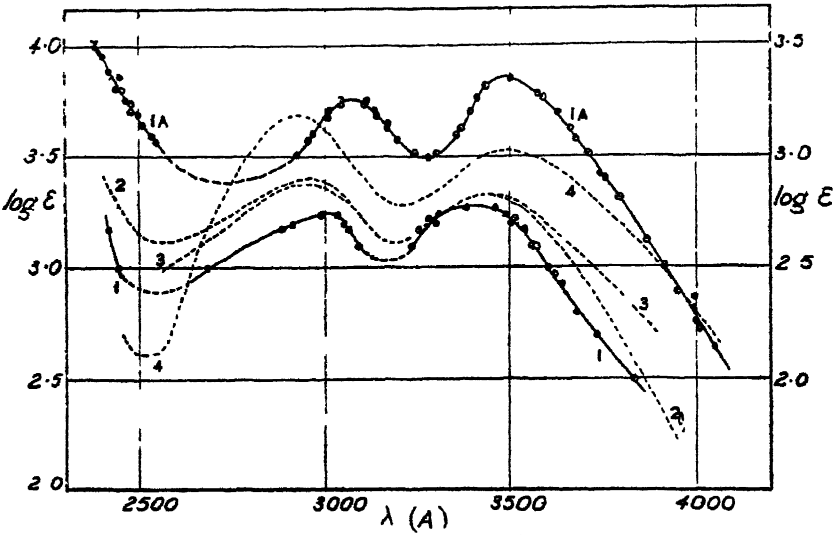

FIG. 1.—Absorption curves of iodoform solutions (C. = $1{\cdot}2 \times 10^{-4} - 2{\cdot}5 \times 10^{-3}$ gm. mols/litre) in alcohol (curve 1), and in cyclohexane (curve 1A). Log ε: left hand scale curves, 1-4; right-hand curve 1A.

TABLE I.

Solvent.	1st Maximum.		2nd Maximum.		Reference.
	$\lambda_{max.}$	log $\epsilon_{max.}$	$\lambda_{max.}$	log $\epsilon_{max.}$	
(a) Iodoform.					
Alcohol . .	3010	3·25	3410	3·30	Curve 1, Fig. 1.
,,	3010	3·25	3410	3·35	Scheibe.[9]
Alcohol . .	2960	3·41	3440	3·32	Curve 3, Fig. 1.
,,	2940	3·5	3450	3·45	Lowry and Sass.[2]
,,	2920	3·7	3500	3·53	Curve 4, Fig. 1.
Cyclohexane .	3070	3·27	3490	3·35	Curve 1A, Fig. 1.
Hexane . .	3070	3·26	3480	3·35	Scheibe.[9]
(b) Methyl Iodoform.					
Alcohol . .	3065	3·26	3400	3·18	Curve 1, Fig. 2.
Cyclohexane .	3110	3·21	3440	3·20	Curve 2, Fig. 2.
(c) Caesium Tri-iodide.					
Alcohol . .	2900	4·60	3600	4·46	Gilbert, Goldstein and Lowry.[3]

(b) Iodoform in Cyclohexane.—Solutions of iodoform in cyclohexane are also sensitive to light and slowly turn violet-pink due to the liberation of free iodine. Since iodine dissolved in cyclohexane has only a weak absorption in the region where iodoform absorbs strongly, we should expect the absorption curve of iodoform in this solvent to be less influenced by the photo-decomposition than that obtained with the alcoholic solution.[*]

The absorption curve of iodoform in cyclohexane is given in Fig. 1 (curve 1A). The data in Table I. show that the position and height of the maxima agree well with those found by Scheibe using hexane as solvent.[†] The measurements were reproducible even when the iodoform solution had become faintly pink after exposure to daylight for half-an-hour. The whole absorption curve of iodoform in cyclohexane is shifted about 60-80 A. towards the visible region compared with the curve in alcohol, but otherwise the absorption is very similar in the two solvents (it should be noted that curve 1A in Fig. 1 is plotted with a different ordinate scale).

(c) Absorption Spectrum of Methyl Iodoform.—Solutions of methyl iodoform are more readily decomposed on exposure to light than solutions of iodoform. By using the procedure described in the case of iodoform it was found possible, however, to prepare colourless solutions of methyl iodoform in alcohol and in cyclohexane and to measure their absorption spectra before any appreciable decomposition took place. The absorption curves are shown in Fig. 2, and the characteristic data are compared in Table I. with the data for iodoform. The absorption curves of the two substances are very similar, but in both the methyl iodoform curves the existence of a third less intense band at about 3800 A. is indicated. On continued exposure of the solution of methyl iodoform in alcohol to light, the two bands became more pronounced, and the values

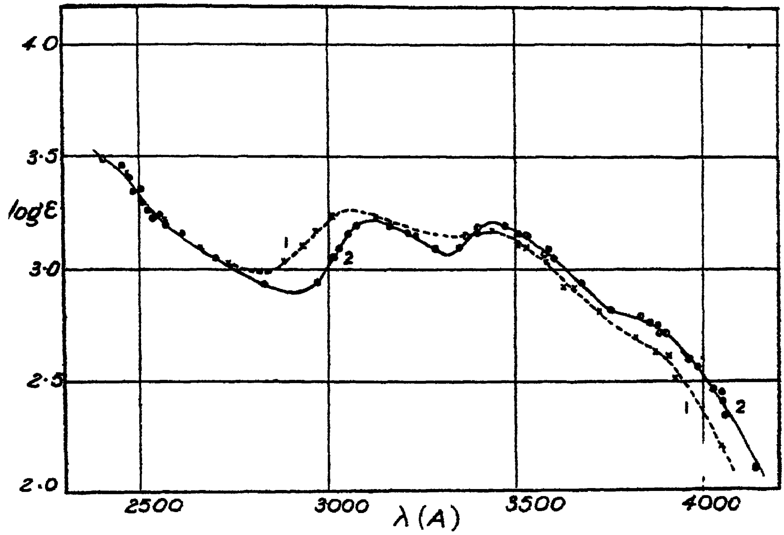

FIG. 2.—Absorption curves of methyl iodoform solutions (C. = $5 \times 10^{-5} - 1{\cdot}2 \times 10^{-3}$ gm. mols/litre) in alcohol (curve 1), and in cyclohexane (curve 2).

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[*] Although the formation of I_3^- cannot take place in a solvent like cyclohexane, there is a possibility that HI_3 may be formed. Absorption measurements were made of solutions in cyclohexane of (*a*) I_2, (*b*) HI, and (*c*) $I_2 + HI$. There was no increased absorption with (*c*) such as would be expected if HI_3 were formed (*cf.* also, Tinkler, *J.C.S.*, 1907, **91**, 996; Warburg and Rump, *Z. Physik*, 1928, **47**, 305).

[†] The extinction curve of iodoform in hexane has recently been measured by Hunter, Qureishy and Samuel (*J.C.S.*, 1936, 1576), who find $\lambda_{max} = 3075$ and 3490 A. Their values of log K_{max} are only about 2·4, but it is not certain whether their K is really the same as ϵ.

of λ_{max} approached those characteristic of the I_3^- ion, exactly as in the case of iodoform. In cyclohexane it was more easy to obtain reproducible results.

The results which have been described for iodoform and methyl iodoform show that the two "iodoform" bands are characteristic of this type of molecule. They are, however, much less intense than those which are characteristic of I_3^-, and the maxima occur at different wave-lengths While there is a qualitative similarity between the absorption of the two types of molecule, the quantitative data show that it does not amount to identity of the absorption curves.

Absorption Spectra of the Tri-iodides of the Phosphorus Group.

The chief difficulties in attempting to measure the absorption curves of solutions of the tri-iodides of this group are due to (*a*) the limited solubility of some of these substances in suitable solvents, and (*b*) the instability of many of the solutions and the consequent uncertainty whether the absorption observed is really due to the molecular species originally dissolved. For the latter reason (*e.g.*, formation of I_3^-) reliable results could not be obtained with alcohol as solvent.

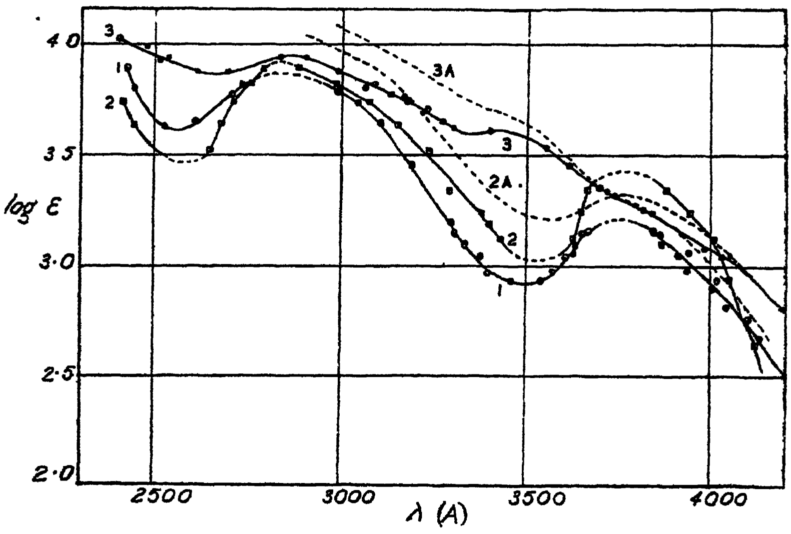

FIG. 3.—Absorption curves of solutions in cyclohexane of PI_3 (curve 1), AsI_3 (curve 2), and SbI_3 (curve 3), and of solutions in benzene of AsI_3 (curve 2A), and SbI_3 (curve 3A).

In the case of phosphorus, arsenic, and antimony tri-iodides, it was possible to measure the absorption curves of the solutions in cyclohexane. With the arsenic and antimony compounds measurements were also made in benzene solution over a more restricted wave-length range. The solutions of these substances in cyclohexane or in benzene are colourless or pale yellow when freshly prepared, but turn pink more or less rapidly due to liberation of iodine. As in the case of iodoform, however, a small amount of decomposition does not appreciably affect the absorption curve in this type of solvent.

The absorption curves of the three tri-iodides are shown in Fig. 3. These curves were obtained with solutions varying in concentration from 0·7-7·0 × 10^{-4} gm. mols/litre. In the case of SbI_3 it was found that below this concentration range Beer's Law is not strictly obeyed—there is a gradual displacement of the whole curve to higher values of log ϵ with increased dilution. Owing to the small solubility of AsI_3 in cyclohexane the practically saturated solution had to be used for the absorption measurements. The characteristics of the absorption curves in cyclohexane are summarised in Table II., and compared with the other data available in the literature regarding the absorption of these tri-iodides in the vapour state and in solution.

TABLE II.

Solvent.	λ_{max}.	log ϵ_{max}.	λ_{max}.	log ϵ_{max}.	λ_{max}.	log ϵ_{max}.
(a) Phosphorus Tri-iodide.						
Cyclohexane .	2850	3·82	—	—	3750	3·2
(b) Arsenic Tri-iodide.						
Cyclohexane .	2840	3·90	—	—	3770	3·4
Benzene .	<3000	~4·0	—	—	3770	3·3
Ether[11] .	2853	—	—	—	3773	—
(Vapour)[14] .	2840	—	—	—	3860	—
(c) Antimony Tri-iodide.						
Cyclohexane .	2860	3·95	~3450	~3·6	~3800	~3·3
Benzene .	<3000	~4·0	~3450	~3·7	~3800	~3·3
Ether[11] .	2875	—	3440	—	—	—
(Vapour)[11] .	2893	—	3500	—	—	—
(Vapour)[11] .	2770	—	3430	—	—	—
(d) Bismuth Tri-iodide.						
Ether[11] .	2830	—	3333	—	—	—
(Vapour)[11] .	2830	—	3350	—	—	—
(Vapour)[14] .	2810	—	3386	—	—	—

Phosphorus, arsenic, antimony and bismuth tri-iodides all have a strong absorption band with λ_{max} at about 2850 A., and from measurements in cyclohexane the intensity of this band seems fairly constant at log $\epsilon_{max} = 3{\cdot}8$ to $4{\cdot}0$. A second well-defined but less intense band with λ_{max} at about 3800 A. occurs in the curves of phosphorus and arsenic tri-iodides, but with antimony iodide its existence is marked by the increased absorption due to a third band at about 3400 A. For bismuth iodide no quantitative data could be obtained, since it is practically insoluble in cyclohexane. The data of Kato and Someno,[11] and of Butkow,[14] however, indicate that the absorption of bismuth iodide is similar to that of the antimony compound.

Comparison of the absorption curves of these tri-iodides in cyclohexane, especially those of phosphorus and of arsenic with the absorption curves of iodoform and of methyl iodoform in the same solvent, shows that all these substances have two absorption bands in the near ultra-violet region with maxima at 2800-3100 and 3400-3800 A. Apart from this general similarity, however, the following differences in the absorption curves of the iodoform and phosphorus tri-iodide groups should be noted :.

(*a*) In the PI_3 group the maxima are at about 2850 and 3800 A., whereas the " iodoform " bands are much closer together at about 3100 and 3500 A.

(*b*) The " iodoform " bands are very nearly equal in intensity (log $\epsilon_{max} \sim 3{\cdot}3$), but in the PI_3 group the shorter wave-length band

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[14] Butkow, *Z. Physik*, 1934, **90**, 810.

(log $\epsilon_{max} \sim 4$) is about five times more intense than the longer wave-length band (log $\epsilon_{max} \sim 3{\cdot}3$).

(*c*) With SbI_3 and BiI_3 the existence of a third band between the two above-mentioned maxima is indicated.

It is seen, therefore, that in all these normal tri-iodides definite differences in the absorption curve can occur, in spite of the general similarity of structure.

Comparison of the Absorption Spectra of Iodides Containing One or More Iodine Atoms.

In conclusion, it is of interest to see how the region of maximum absorption varies in the ultra-violet absorption spectra of covalent iodides as the number of iodine atoms attached to one common atom increases. With iodides in the gaseous, liquid or dissolved states, the continuous absorption spectrum may show either one or two maxima, the positions of which appear to depend mainly on the number of iodine atoms which are linked to one common atom in the molecule.[15] As the number of iodine atoms is increased, there is a gradual displacement of the region of maximum absorption to higher wave-lengths. This is particularly well shown in the series methyl iodide, methylene iodide, and iodoform,[2,16] and corresponds to a progressive loosening of the whole molecule in this series.*

From the results described in this paper, along with previously recorded data, it can be stated that practically all molecules containing either three or four iodine atoms linked to one central atom have two absorption bands in the near ultra-violet region 2800 to 4000 Å. The maxima of these bands do not correspond exactly to those given by iodoform, but vary according to the nature of the central atom. The positions of the two maxima for many such molecules (*cf. e.g.* PI_3 and AsI_3) are fairly constant, however, at about 2800-2900 and 3700-3800 A., respectively, and only slightly influenced by the nature of the atom to which the iodine atoms are bound. The bands occur, for example, in neutral molecules such as phosphorus tri-iodide or stannic iodide [17,18] or even in complex ions of the TlI_3^{--} or PbI_4^{--} type.[19]

As regards the primary light absorption process, there is a considerable amount of spectrographic and photo-chemical evidence that with non-ionised iodides, the light absorption in the region 2000 to 4000 Å. results in a dissociation of the molecule with the production of free iodine atoms.

The alkali iodide vapours, for example, show two absorption maxima at 3240 and 2580 Å., which can be attributed to dissociation giving iodine atoms in the normal ($^2P_{3/2}$) and first excited ($^2P_{1/2}$) states, respectively. The frequency difference of the two maxima ($\Delta\nu = 8000$ cm.$^{-1}$) corresponds very closely with the energy of excitation of the iodine atom $^2P_{1/2} - {}^2P_{3/2} = 7600$ cm.$^{-1}$). With the alkyl iodides on the other hand,[21] only the maximum at about 2600 Å. occurs, both for the gaseous state and in solution, and can be attributed to a dissociation giving $^2P_{1/2}$ iodine atoms.

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[15] Butkow, *Acta Physicochim. U.R.S.S.*, 1935, 3, 205.

[16] Henrici, *Z. Physik*, 1932, 77, 35.

* The preparation of CI_4 and the measurement of its absorption spectrum were attempted, but it is too unstable in solution to give reliable results ; *cf.* also Lowry and Sass (*loc. cit.*,[2] p. 628).

[17] Grant, *Trans. Faraday Soc.*, 1935, 31, 433.

[18] Banov, *Acta Physicochim.*, *U.R.S.S.*, 1935, 2, 733.

[19] Fromherz and Kun Hou-Lih, *Z. physikal. Chem.*, *A*, 1931, 153, 321.

[20] Schmidt-Ott, *Z. Physik*, 1931, 69, 724.

[21] Herzberg and Scheibe, *Z. physikal. Chem.*, *B*, 1930, 7, 390.

In the case of tri-iodides the frequency differences of the two bands is always about 5600 (*e.g.* CHI_3) to 8700 cm.$^{-1}$ (*e.g.* PI_3). Although this frequency difference does not correspond exactly in every case with the energy of excitation of the iodine atom, it is reasonable, as has been suggested elsewhere [7,15] to relate the two maxima to dissociation giving $^2P_{3/2}$ and $^2P_{1/2}$ iodine atoms (with molecules like SnI_4 and BiI_3 illuminated by ultra-violet light of shorter wave-length (about 2500-2100 Å.) a dissociation in which an activated I_2 molecule is eliminated in one act is possible).[22] For covalent iodides containing two iodine atoms bound to a common atom, fewer absorption spectrum data are available, but it seems that in general only one maximum exists in the region under discussion. This maximum occurs in the wave-length range 2600 to 3000 A.,* *i.e.* intermediate between the maxima for mono- and tri-iodides, respectively, which correspond to dissociation giving exited $^2P_{1/2}$ iodine atoms.

Note *added in proof* (*10th February*, 1937): A paper has just been published by C. B. Allsopp on the absorption spectra of tri-iodides (*Proc. Roy. Soc.*, 1937, **158,** 167). His conclusions regarding the primary processes associated with the two absorption bands of tri-iodides containing covalently bound iodine are essentially the same as those in our paper. It is doubtful, however, whether the intensities of the two bands of the tri-iodides of As, Sb, and Bi shown in Fig. 1 ($\log \epsilon_{max} \sim 4$) are really characteristic of these molecules.

Summary.

(1) The absorption spectra of iodoform and of methyl iodoform in alcohol and in cyclohexane have been measured for the wave-length range 2000-4000 A.

(2) The absorption curves of both substances are very similar to one another and differ from the curve characteristic of I_3^-.

(3) The absorption spectra of PI_3, AsI_3 and SbI_3 in cyclohexane have been measured and compared with that of iodoform.

(4) The results are discussed in relation to the absorption of iodides in general.

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[22] Terenin, *Compt. Rend. Acad. Sci. U.R.S S.*, 1935, **1**, 482

* *E.g.* mercuric [15] iodide 2700, methylene [2] iodide 2960.

I. THE OSMOTIC PRESSURE OF GUM ARABIC. PART III.—THE IONISATION OF SODIUM, CALCIUM AND ACID GUMS.

By Henry Bowen Oakley.

Received 15*th December*, 1936.

In a preceding paper [1] the object was to eliminate the ionic osmotic pressure of gum-arabic in order to determine its molecular weight. In the present paper the object is to determine the maximum osmotic pressure in the absence of electrolyte in order to measure the effective degree of ionic dissociation of the gum, and to see how this varies with concentration. D. R. Briggs [2] has also studied the osmotic pressure of gum arabic in salt solutions but as he was interested in the distribution of the salt rather than in the behaviour of the gum in pure water his results do not bear on the subject of this paper.

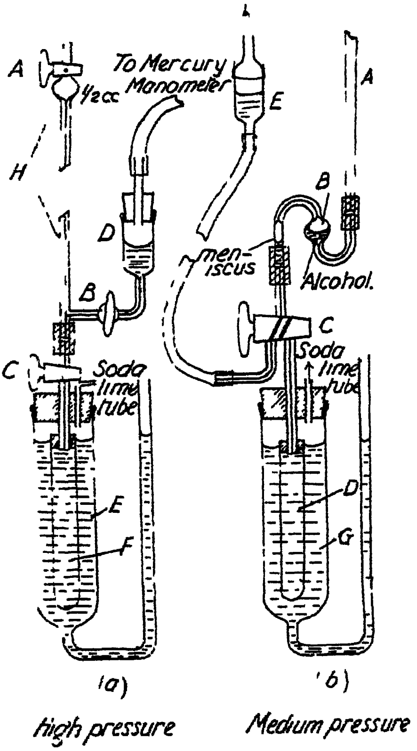

Fig. 1.—Osmometers.

Apparatus.

The two forms of osmometer used are illustrated in Fig. 1, (*a* is used for pressures of 3 to 100 cms. of mercury and (*b*) for pressures of 5 to 50 cms. of water. In (*a*) taps C and A are closed and the air in the capillary and bulb H, are compressed by applying air pressure from a mercury manometer on to the surface of the water in D. The approximate pressure is found by trial and error by closing B and opening C when the water in the capillary will move up or down according to whether the applied pressure is too small or too large. The bulb must be well shielded from sudden changes of temperature. For high pressures the bulb must be filled with compressed air before extra pressure is applied through D. Finally the arrangement is allowed to reach equilibrium with B closed and C open. C is then closed and D opened and the manometer adjusted to give the same height of water in the capillary. To the manometer reading must be added the pressure represented by the difference in levels between the water in D and in the outer vessel E.

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[1] H. B. Oakley, *Trans. Faraday Soc.*, 1936, 32, 1360.
[2] D. R. Briggs, *J. Physic. Chem.*, 1934, 38, 1145.

The advantage claimed for this arrangement is that the pressure can build itself up gradually to an equilibrium value with a minimum of change in volume, and repetition of pressure readings can be made without disturbing the tension in the collodion sac F. This is an important point when high pressure are being measured owing to the considerable elasticity of the sac; furthermore a finer capillary can be used, which greatly expedites the attainment of equilibrium.

In osmometer (*b*) a fine alcohol manometer AB, is used, this is connected to the sac D by the two-way diagonally bored tap C. When equilibrium has been attained the tap is turned to connect it with the levelling tube E, which is then adjusted to bring the alcohol level in A to its previously ascertained equilibrium position. The difference in levels of water in E and the outside vessel G is then measured by means of a cathetometer or scale.

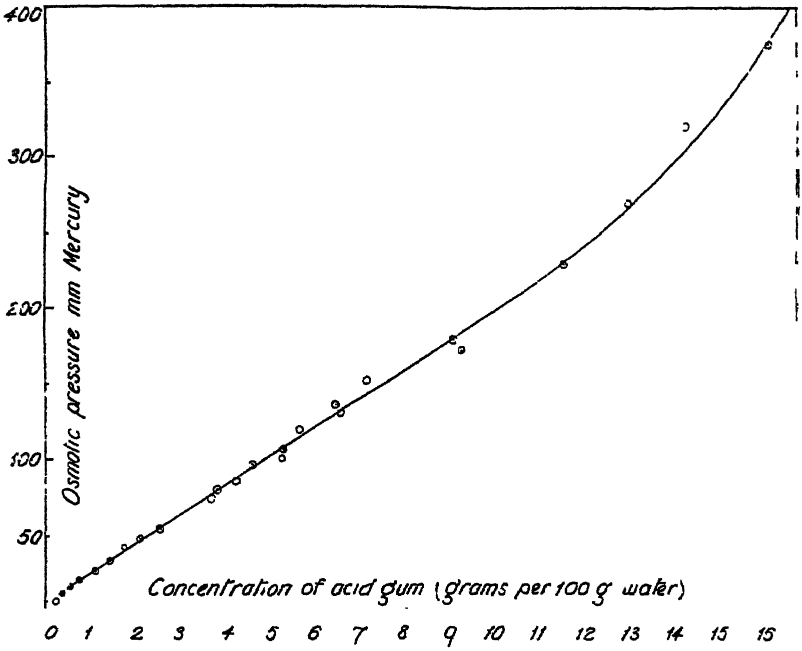

FIG. 2.

Owing to the fineness of the capillary this arrangement is sensitive to changes in air temperature and a great improvement could be effected by designing the apparatus so that it could be immersed in the thermostat over the bulb B.

Similar advantages are claimed for this apparatus as for the previous one with the addition that a very fine capillary is even more important here because of the much smaller pressures concerned in attaining equilibrium. The use of alcohol in such a fine capillary eliminates the liability to large capillary errors which may occur with water.

In both forms the tap is fitted with 1 mm. bore tubing so that diffusion of the colloid is not important. In any case the concentration is determined by analysing the contents of the sac at the end of the experiment after rejecting the first few drops emerging from it.

All measurements were made at 25° and the outer liquid was protected from CO_2.

Osmotic Pressure of Acid Gum.

In Fig. 2 is plotted the osmotic pressure of electrodialysed (acid) gum against water. As shown previously [3] the acid gum is not stable, although its decomposition is slow at 25°. This has also been noticed by Amy [4] although it apparently was not known to Briggs [5] or Pauli and Ripper,[6] and other investigators. This fact was fully confirmed by the present experiments. When a newly electro-dialysed sample of gum is introduced into the osmometer the pressure rises to a certain value and then slowly falls. If the outside water is changed the pressure again rises but to less than its former value and then falls again and this may be repeated indefinitely. At the same time a small quantity of material passed through the membrane. For this reason the experimental error is rather large, although by noting the maximum pressure after changing the water and measuring the concentration immediately afterwards a fairly good straight line has been obtained. It is notable that this line when produced does not pass through the origin but cuts the pressure axis at about 8 mm. mercury; the meaning of this will be discussed later.

During this process of dialysis the equivalent weight of the gum appears to undergo a progressive increase as determined by titration of samples with $N/10$ NaOH and methyl red.

Period of dialysis.	*Equivalent Wt.*
0 days	1180
8 ,,	1300
10 ,,	1340
13 ,,	1433
15 ,,	1560

To test whether this change was accompanied by a change in molecular weight a sample of the dialysed gum was converted to the calcium salt and its osmotic pressure measured in $N/10$ $CaCl_2$. The value of P/C with progressive dilution did not attain a constant value but continued to fall some 30 per cent. below the figures obtained for normal calcium gum,[1] suggesting that diffusible material was present.

Although Amy [4] supposes that acid gum is completely unstable yet his dialysis experiment only showed that this was the case at 100° C. The fact that a solution of acid gum can be kept for a considerable time and yet only show some 10 per cent. of diffusible material suggests that there is an equilibrium between the large gum molecules and its products of degradation. To test this, the products of dialysis were concentrated and neutralised with $Ca(OH)_2$ giving an equivalent weight of 1020. The solution was then dialysed and the osmotic pressure measured in $N/10$ $CaCl_2$. During dialysis about 40 per cent. of the original material passed through the membrane, the remainder gave the following osmotic pressures. This corresponds to a mean "molecular weight" of 120,000.

Although the experiment is not very conclusive, it seems to show that products of auto-hydrolysis of the acid gum can recombine to form substances of high molecular weight. Calcium gum prepared from newly electrodialysed gum has an osmotic pressure corresponding to twice this molecular weight.[1]

Osmotic Pressure of Dialysate of Acid Gum.

C.		
0·637	16·1	25·3
0·47		22·6
0·327	7·0	

Comparison with Gum Partially Hydrolysed with HCl.

I showed previously [3] that $N/50$ HCl partially hydrolyses electrodialysed gum. 10 c.c. of an 8 per cent. solution of acid gum was dialysed

[3] H. B. Oakley, *Trans. Faraday Soc.*, 1935, **31**, 136.

[4] Lucien Amy, *Ann. Chemie*, 1934, **2**, 295.

[5] D. R. Briggs, *J. Physic. Chem.*, 1934, **38**, 867.

[6] Wo. Pauli and E. Ripper, *Koll. Z.*, 1933, **62**, 162.

for three days against $N/50$ HCl at 25°. It was then dialysed against water until there was no reaction for chloride. Its equivalent weight was then the same as the original electrodialysed gum, *i.e.*, 1180. The osmotic pressure of its calcium salt in $N/10$ $CaCl_2$ gave the following results (see table opposite).

This corresponds to a "molecular weight" of 180,000. Since both the equivalent weight and osmotic behaviour approximate to that of the original gum and are very different from the gum after prolonged dialysis against water it may be concluded that HCl slowly breaks down the gum completely and that the products of decomposition escape through the membrane while the spontaneous breakdown of the acid gum produces a different product.

C.	*P.*	*P/c.*
2·20	38·2	17·4
1·66	26·2	15·8
1·26	17·8	14·2
0·86	11·8	13·7
0·59	8·4	14·2

The Osmotic Pressure of Gum with Different Bases.

The osmotic pressure curves of Li, Na, K and Ca gums are shown in Fig. 3. In addition, there is shown the effect of adding NaCl in con-

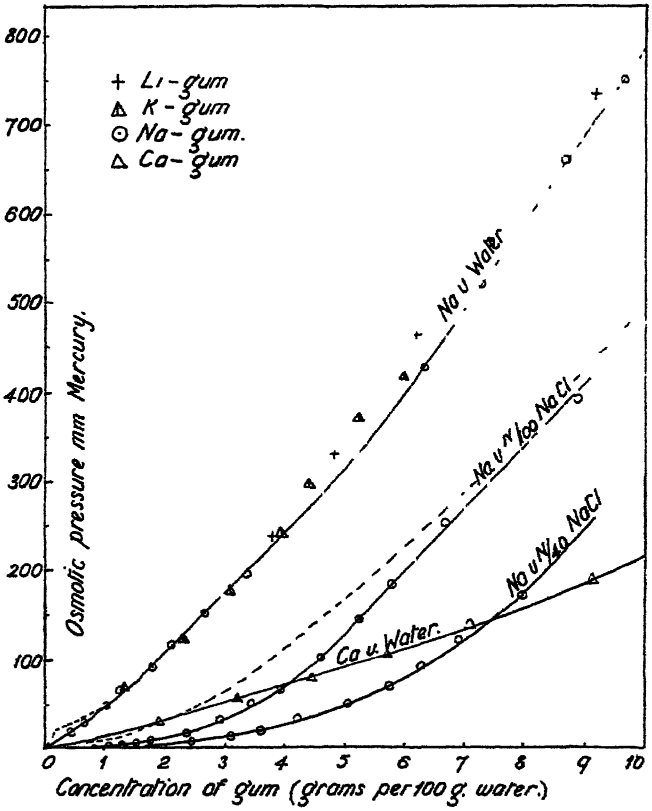

FIG. 3.

centrations of $N/100$ and $N/40$, while the dotted curve shows the theoretical values with $N/100$ NaCl, assuming 50 per cent. ionisation of the gum and complete ionisation of the NaCl calculated according to the simple (ideal theory of the Donnan membrane equilibrium.

The values for lithium, sodium and potassium below a concentration of 4 per cent. lie close together and it seems possible that the rather lower values of sodium at the higher concentrations may be partly due to error caused by loss of sodium through membrane hydrolysis. It was attempted to prevent the loss by making all measurements in $N/100,000$ solutions of the hydroxide of the base concerned, but it was noticed that in the course of an hour the solution failed to colour phenol phthalein and the same effect could be repeated by any number of renewals of the dilute alkali It appears, therefore, that the collodion membrane has the capacity of neutralising alkali and therefore any hydroxide formed by membrane hydrolysis may be immediately neutralised on its formation near the surface of the membrane.

In order to test this, a sac of collodion was reduced to cellulose by treating with alcoholic ammonium sulphide as described by Kasson and Dorr.[7] It was found that this membrane caused no neutralisation of dilute alkali over a period of several days. Experiments were made with sodium gum prepared from electrodialysed gum which therefore did not require to be dialysed free from NaCl. The results are plotted in Fig. 4 on a large scale and are shown by dots in Fig. 3. The curve connects up smoothly with the previous results which would seem to indicate that no great error has been introduced by hydrolysis except at the lowest concentrations. The curve is almost straight up to a concentration of 0·2 per cent. and then decreases its slope rather suddenly, continuing straight to a concentration of 0·7 per cent. and then begins to rise more rapidly. Although it was impossible to carry measurements with acid gum to such low concentrations the two curves agree in that when produced from concentrations above 0·3 per cent. they both cut the pressure axis instead of passing through the origin.

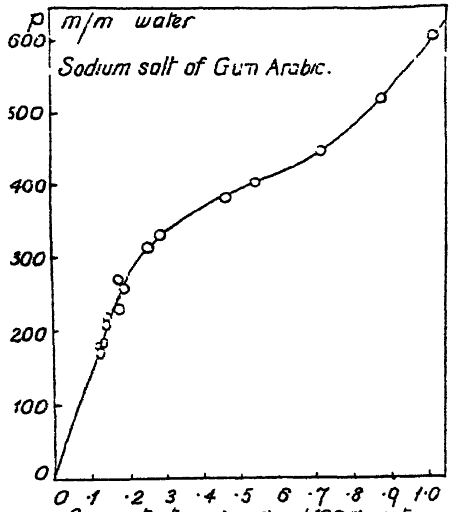

FIG. 4.—Sodium salt of Gum Arabic.

The data illustrated in Figs. 2, 3 and 4 may be used to calculate the number of ions dissociated per molecule of gum, *i.e.* the effective electrovalency n_e and also the apparent percentage ionisation α from the equation

$$P = RT\,(\alpha n + 1)\,.\,10c/M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Where M = molecular weight = 240,000,
n = maximum valency = M/equivalent weight
= 240,000/1200 = 200,
c = concentration in grams/100 c.c. water,
$\alpha n = n_e$.

This has been done in Tables I. and II. Table I. includes values for Na-gum in the presence of $N/100$ NaCl, calculated from the equations of the simple theory of the Donnan membrane equilibrium. The apparent ionisation seems to be nearly the same as in water above a concentration of 3 per cent. Table II. gives values for the lower concentrations of Na-gum.

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[7] Kasson and Dorr, *J. prakt. Chemie*, 1925, **108**, 169.

TABLE I.

	Acid Gum.		Ca-Gum.		Na-Gum.		Na-Gum N/100 NaCl.
c.	n_e.	α.	n_e.	α.	n_e.	α.	α.
10	24	12·1	51	25·5	100	50·0	—
7	25	12·5	48	24·0	88	44·1	46
5	26	12·8	45	22·3	82	41·0	42
3	26	13·1	40	20·2	72	36·0	34
2	27	13·7	38	19·1	69	34·3	30
1	30	15·1	36	18·0	60	30·0	24
0·5	34	16·8		—	76	38·0	—

The following features may be noticed. The ionisation of the acid gum is the lowest and only rises slowly down to a concentration of 1 per cent. The ionisation of the sodium gum is the highest and passes through a minimum at 0·8 per cent., rising rapidly at lower concentrations. It is of interest to note that an effective valency or charge as high as 136 is recorded, *i.e.* the osmotic pressure due to colloid particles is only 1/136 of the total pressure in pure water.

The ionisation of the calcium gum is about half that of the sodium gum and might be expected to pass through a minimum at a much lower concentration, but no data with a cellulose membrane have been obtained.

TABLE II.—SODIUM GUM.

c.	n_e.	α.
1·0	60	30
0·8	58	29
0·6	66	33
0·4	86	43
0·26	116	58
0·21	130	65
0·19	132	66
0·15	134	67
0·10	136	68

This elementary treatment of the results according to the ideal laws of dilute solutions serves little more than as a convenient method of comparison of the data.

In the case of actual dilute solutions, equation (1) must be written in the form

$$P = gRT\,(\alpha n + 1)\,\frac{10\,c}{M} \quad . \quad . \quad . \quad . \quad (2)$$

where g denotes the Bjerrum osmotic coefficient. If we define a quantity g' by the equation,

$$P = g'RT\,(n + 1)\,\frac{10\,c}{M} \quad . \quad . \quad . \quad . \quad (3)$$

then $\frac{g'}{g} = \frac{\alpha n + 1}{n + 1} = \frac{200\alpha + 1}{200 + 1}$, in the present case. We may write therefore $g' = g(\alpha + \frac{1}{200})$ with good approximation, and if α is large compared with $\frac{1}{200}$, we may write with not so high approximation, $g' = g\alpha$.

The quantity g', so defined, takes account both of incomplete ionisation (α) and also of the Bjerrum coefficient (g) which symbolises all departures from the laws of ideal dilute solutions, due to inter-ionic forces, etc. At infinite dilution, $\alpha = 1$, $g = 1$, $g' = 1$. With increasing concentration g will decrease, rapidly at first and then more slowly, and this will tend to produce a corresponding decrease in g'. Increasing concentration will also cause at first a decrease in α, and this will tend to produce a corresponding decrease in the value of g'.

In Fig. 5, g' has been plotted against the square root of the concentration; a pronounced minimum occurs at a concentration of 0·0067 N (0·8 per cent.) For the purpose of comparison there has also been plotted the equivalent conductivity Λ for sodium gum taken from Briggs'[5] figures. A shallow minimum for the quantity occurred at about the same concentration (0·002N or 0·25 per cent.) with lithium, potassium, and calcium gums, but there was no minimum with acid gum. On the other hand Amy[4] found no minimum for sodium gum, but since Briggs obtained evidence for its existence on four different gum compounds it seems to have a sound experimental foundation.

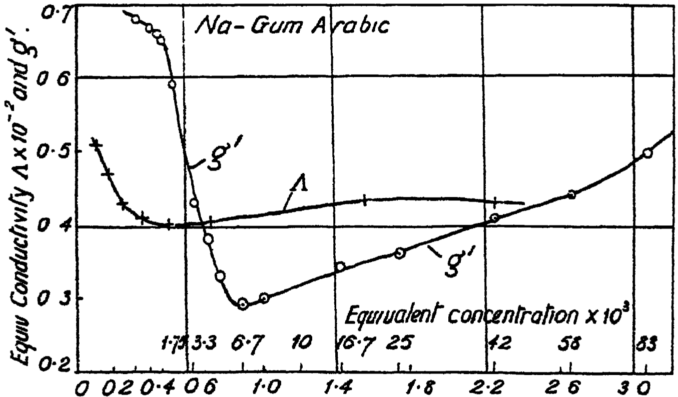

FIG. 5.—Na-Gum Arabic.

Returning to equation (3), by differentiation we have:

$$\frac{dg'}{dc} = \left(\alpha + \frac{1}{100}\right)\frac{dg}{dc} + g\frac{d\alpha}{dc} \quad . \quad . \quad . \quad . \quad (4)$$

So long as dg/dc and $d\alpha/dc$ are both negative dg'/dc will also be negative and no minimum can occur. Since dg/dc can never become positive let us suppose we reach a region of c where α attains a minimum; thereafter $d\alpha/dc$ become positive. The corresponding minimum of g' will then occur when the numerical values of $g d\alpha/dc$ and $(\alpha + 1/100)\, dg/dc$ are equal. If, as is probable, this occurs in a region where g is only decreasing slowly it is not necessary that the rate of increase in ionisation $d\alpha/dc$ should be large since g and α are of the same order of magnitude.

The hypothesis of an increase of ionisation with increasing concentration has been recently put forward with strong experimental and theoretical justification by Hartley,[11] Collie and Samis to explain the conductivities and transport numbers of various paraffin chain salts and it is probable that this explanation can also be applied to the rise of g' in this case. In this connection it is of interest to compare the distance between the particles with the diameter of the particle at the two concentrations at which the conductivity (0·25 per cent.) and the coefficient g' (0·8 per cent.) begin to rise. This difference in the position of the two minima will be referred to later.

The author [10] has recently calculated that the diameter of a hydrated particle of Na-gum of "molecular" weight of 240,000 is 11 mμ. The relevant calculations are given in the following table :—

Per cent. Gum	0·25	0·8
Equivalent concentration per litre . .	0·0021	0·0067
Distance between centres of molecules .	55 mμ	37 mμ
Distance between surfaces of molecules .	44 mμ	26 mμ
Ratio of distance between surfaces to diameter	4·0	2·4

The last figures in this table indicate that the particles are separated by four times their diameter when the equivalent conductivity begins to rise, and by only 2·4 times their diameter when the osmotic pressure coefficient begins to rise. The depth of the diffuse double layer or ionic atmosphere is unknown, but it does not seem improbable that the distribution of gegenions should suffer interference within these distances.

A serious difficulty arises however in accounting for the part of the curve at concentrations below that at which the minimum occurs if the degree of aggregation of the gum particle is regarded as being constant down to the lowest concentrations. If this were the case g' should fall most rapidly at the lowest concentration and less rapidly as the minimum was approached. The course of the curve is much more in accordance with what would be expected if the gum consisted of smaller units of single or low electrovalency at concentrations below 0·25 per cent. and suddenly aggregated to large micelles above this concentration. This behaviour would be analogous to that of the paraffin chain salts elucidated by Hartley. An objection to this hypothesis is that the osmotic data obtained in the presence of $N/50$ NaCl or higher concentrations give no evidence for a decrease of aggregation down to a concentration of 0·1 per cent. of gum. It is conceivable that dissociation is prevented by the presence of electrolyte until a much lower concentration is reached and that in the absence of electrolyte association to micelles only starts at a concentration of about 0·2 per cent. where the steep part of the curve begins.

Another difficulty is to account for the different positions of the minima in Λ and g'. Why the conductivity should increase earlier than the osmotic coefficient is not clear, unless it can be attributed to an increase in a kind of "surface conductivity" contributed by those ions nearest the surface of the particle. Such ions might be free to move tangentially to the surface under an electric field and yet be hindered from moving radially by the attraction of the particle itself; the latter restriction might also restrict the osmotic pressure. It is noteworthy that the concentration at which Λ is a minimum is also about the concentration at which the slope of the osmotic pressure curve in Fig. 4 decreases rather suddenly. The data however should be confirmed on a single stock of gum.

The Hydrogen Ion Activity of Acid Gum.

Finally it is of interest to compare the published figures for the hydrogen ion activity of acid gum determined by the hydrogen electrode, with the figures of the hydrogen ion concentration calculated from the osmotic data (osmotic activity). These have been plotted in Fig. 6.

It will be seen that Pauli and Ripper's figures [6] have a tendency to be noticeably higher than those of Briggs,[5] and that both are much higher than the calculated osmotic activity up to a concentration of 6 per cent. Above this the curves cross. The fact that the electrochemical affinity is higher than the osmotic activity is in accordance with repeated observations by Briggs,[2] Hammersten,[9] and others that an electrometric determination of the distribution of ions between a colloid and a solution across a membrane always leads to a calculated value of the osmotic pressure which is much higher than the experimental value. This has been known as the Hammersten effect and Briggs calls it anomalous, but Hartley[11] points out, however, that no simple direct relationship exists between the osmotic and mean activity coefficients, and also that the interpretation of the E.M.F. of cells with a liquid junction is particularly uncertain when there is a large difference in the electrovalency of the ions.[8]

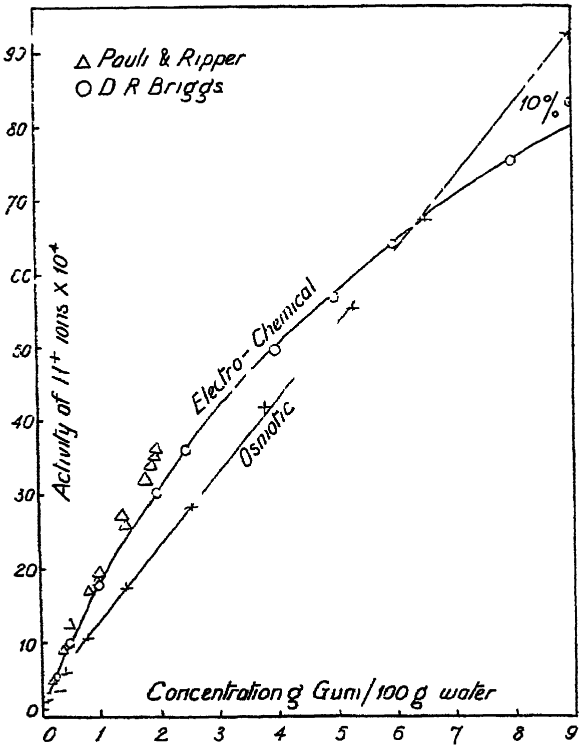

Fig. 6.

I desire to express my sincere thanks to Professor F. G. Donnan for his encouraging interest in this work, and to Messrs. Unilever Ltd. for a grant which enabled it to be carried out.

Summary.

1. The osmotic pressure of acid gum arabic and of the sodium, potassium, lithium and calcium salts have been measured up to a concentration of 10 per cent. of gum.

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[8] G. S. Hartley, B. Collie and C. S. Samis, *Trans. Faraday Soc.*, 1936, **32**, 795.

[9] E. Hammarsten, *Biochem. Z.*, 1924, **144**, 383.

[10] H. B. Oakley. *Biochem. J.*, 1937, **31**, 28.

[11] G. S. Hartley, *Trans. Faraday Soc.*, 1935, **31**, Footnote p. 32 and Fig. 5.

2. The pressure-concentration curve of Na-gum shows a sudden increase of slope below a concentration of 0·25 per cent. and a similar effect is shown by acid gum. Data for the other gum salts at such low concentrations have not been obtained. The possibility of explaining this by dissociation of the gum particle is discussed.
3. The apparent ionisation calculated from the results passes through a minimum. This is attributed to change of activity and a subsequent increase of ionisation due to the overlapping of the atmospheres of gegenions. The maximum electrovalency is 200 (Particle wt., 240,000).
4. 5 per cent. solutions have the following effective electrovalencies per particle: Ca-gum 25; H 26; Na, K, Li, 82 to 90.
5. A qualitative correlation of these results with the conductivity data of D. R. Briggs has been discussed.
6. It has been shown that the osmotic "activity" of the hydrogen ions of the acid gum is much lower than the corresponding electro-chemical activity (as published) up to 6 per cent. concentration.

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RESONANCE IN UREA AND ITS DERIVATIVES —PART I.—DIAMAGNETICS.

By Archibald Clow

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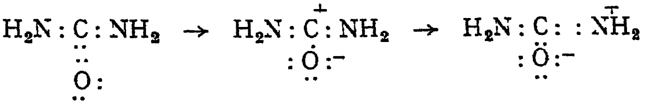
Several structures have been proposed to explain the physical and chemical properties of urea, from carbamide to the cyclic structure proposed in 1913 by Werner.[1] Since that date a continuous series of investigations on crystal structure, diamagnetism, Raman spectra, etc., has contributed to various aspects of the problem, but most of them have lacked conclusiveness in that they have not considered the structures of urea derivatives as well as of urea itself, a fact that has led to considerable confusion in their interpretation. Of the few extensive researches on urea derivatives those of de Beer, Buck, and Hjort[2] on the anæsthetic effect of some seventy substituted ureas might be mentioned. Although de Beer and his co-workers do not discuss the relation between anæsthetic effect and structure a correlation can be shown between their results and those to be described.

With the introduction of the concept of quantum mechanical resonance, Pauling[3, 4] suggested that urea and some of its derivatives should be represented by resonance structures,



$$\mathrm{H_2N:\underset{\substack{\cdot\cdot\\ \cdot\cdot\\ O:\\ \cdot\cdot}}{C}:NH_2} \rightarrow \mathrm{H_2N:\underset{\substack{:\ddot{O}:^-\\ \cdot\cdot}}{\overset{+}{C}}:NH_2} \rightarrow \mathrm{H_2N:\underset{\substack{:\ddot{O}:^-\\ \cdot\cdot}}{C}::\overset{+}{N}H_2}$$

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[1] Werner, *J.C.S.*, 1913, **103**, 1010.
[2] De Beer, Buck and Hjort, *J. Pharm.*, 1934, **52**, 216; 1935, **54**, 188.
[3] Pauling, *Proc. Nat. Acad. Science*, 1932, **18**, 293.
[4] Pauling and Sherman, *J. Chem. Physics*, 1933, **1**, 606.

having resonance energies for example :—

Urea	1·59 ev.
N . N′-Diphenyl-urea . . .	0·55 ev.
N . N-Diphenyl-urea	0·50 ev.

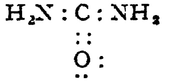
Thermal data are not available for partially ionic bonds thus preventing a detailed analysis of resonance by the method initiated by Pauling. Clow and Thompson,[5] however, have demonstrated that diamagnetism can give accurate information about the possible states of a resonating molecule, e.g., $:\overset{+}{O}:::C:\underset{\cdot\cdot}{\overset{\cdot\cdot\,-}{O}}: \rightleftharpoons :\underset{\cdot\cdot}{\overset{\cdot\cdot\,-}{O}}:C:::\overset{+}{O}:$, and the time spent in these states, the theoretical diamagnetisms being calculated by the method formulated by Gray and Cruickshank.[6]

Diamagnetism is now applied to the resonance structures of urea and its derivatives where it brings out the overwhelming effect of substitution on the structure of the parent molecule, which should help to clarify existing data for these compounds.

Experimental and Calculations.

The susceptibilities of the ureas, purified by repeated recrystallisation, were measured at 18° C. with the Curie Chéneveau magnetic balance which has already been described,[7] constancy of susceptibility being taken as the criterion of purity rather than melting-points about which there is considerable confusion in the literature. All susceptibilities are relative to pure water $\chi = -0{\cdot}72 \times 10^{-6}$ and throughout the discussion they have been multiplied by -10^{-6}.

The calculation follows that of Gray and Cruickshank; the calculation of the susceptibility of carbamide alone being given here, as all the others follow the same general principles. :—



$$\begin{array}{c} H_2N:C:NH_2 \\ :: \\ \underset{\cdot\cdot}{O}: \end{array}$$

From the residual charges due to the unequal sharing of bond electrons as given by Sidgwick[8] the atoms in carbamide are found to have the residual charges: C $+0{\cdot}54$, H $+0{\cdot}29$, O $-0{\cdot}42$, N $-0{\cdot}64$. To these residual charges is assigned the significance given to them by Gray and Cruickshank, namely the fraction of time in which the atom has the neighbouring whole number charge for which the ionic diamagnetism can be calculated[9] from

$$= -1{\cdot}976 \times 10^{-6} \sum_{K} \frac{n_x^4}{(Z - S_x)^2}\left[1 - \frac{3l_x(l_x + 1) - 1}{5n_x^2}\right],$$

i.e., $C^{-0.54}$ is equivalent to the carbon atom being 54 per cent. of the time in C^{-1} state and 46 per cent. in C°. This gives for carbamide a susceptibility 43·58, which however neglects the depression of diamagnetism that takes place on bond formation, equal to 16·12 for carbamide

$$[1(C::O) = 10{\cdot}28,\ 2(C:N) = 3{\cdot}56,\ 4(N:H) = 2{\cdot}28].$$

Subtracting this from 43·58 gives the theoretical susceptibility of carbamide 27·46. The calculation of the other susceptibilities is similar. Table I. gives the experimental susceptibilities of the ureas discussed.

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[5] Clow and Thompson, *Nature*, 1936, **138**, 802.
[6] Gray and Cruickshank, *Trans. Faraday Soc.*, 1935, **31**, 1491.
[7] Gray, Clow and Cruickshank, *J. Sci. Inst.*, 1936, **13**, 13.
[8] Sidgwick, *Covalent Link in Chemistry* (1933), p. 154.
[9] Pauling, *Proc. Roy. Soc.*, *A*, 1927, **114**, 181.

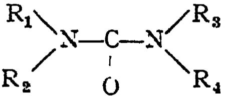
TABLE I.—ALL THE KNOWN SUSCEPTIBILITIES OF SUBSTITUTED UREAS ARE COLLECTED TOGETHER IN THIS TABLE.

Urea.	Susceptibility.		
	Clow.	Pascal.	Devoto
Urea	33·66	33·60	33·40
N-Methyl-urea	44·62	36·72	42·40
N-Methylol-urea	46·33	—	—
N-Ethyl-urea	—	—	55·50
N-Propyl-urea	—	—	67·40
N-Phenyl-urea	79·80	81·09	—
N . N-Dimethyl-urea	53·62	—	55·10
N . N-Diphenyl-urea	126·3	—	—
N . N′-Dimethyl-urea	60·03	—	56·30
N . N′-Dimethylol-urea	68·00	—	—
N . N′-Diethyl-urea	74·07	—	—
N . N′-Diphenyl-urea	127·6	132·7	—
N-Methyl-N′-phenyl-urea	—	93·35	—
N . N-Diethyl-N′-phenyl-urea	—	126·4	—
N . N-N′-Triphenyl-urea	—	176·5	—
N . N-N′ . N′-Tetramethyl-urea	75·70	—	—
N . N-N′ . N′-Tetraethyl-urea	—	—	122·4
N . N′-Dimethyl-N . N′-diphenyl-urea	148·9	—	—

Discussion.

(a) Tetra-substituted Ureas.

Considerable clarity will be gained by first considering the urea molecule in its completely substituted form because there is no doubt about the structure of the parent molecule when so substituted, *viz.*



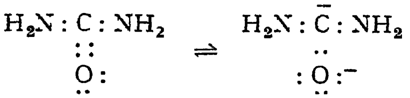
In this form the only possible resonance is in the $C::\ddot{O}:$ group, but as there is no molecule in which a resonance such as $C::\ddot{O}: \rightleftharpoons \overset{+}{C}:\underset{\cdot\cdot}{\overset{\cdot\cdot\,-}{O}}:$ is prohibited the calculation of the diamagnetic susceptibility will already involve this resonance, which can therefore be neglected. On these grounds the susceptibility calculated for a tetra-substituted carbamide should be in agreement with the experimental susceptibilities of these compounds. This is so.

	Exp.	Calc.
N . N′-N . N′-Tetramethyl-urea	75·7	74·9
N . N′-N . N′-Tetraethyl-urea [10]	122·4	122·26
N . N′-Dimethyl-N . N′-diphenyl-urea	148·9	149·44

These measurements show that where a carbamide structure is certainly present the diamagnetic susceptibility demonstrates its presence without doubt, showing, with the other physical properties of these compounds, low melting-point, distillation without decomposition, the presence of a non-polar molecule

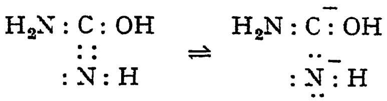
b) The Urea Molecule.

The unsubstituted urea molecule presents a much more complicated system than its tetra-substituted derivatives on account of the greater number of possible resonant structures. The carbamide structure as already mentioned can resonate between



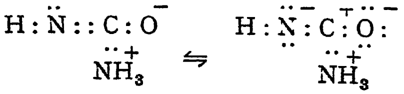
$$\underset{\substack{::\\ O:\\ \cdot\cdot}}{H_2N : C : NH_2} \rightleftharpoons \underset{\substack{\cdot\cdot\\ :O:^-\\ \cdot\cdot}}{H_2N : \bar{C} : NH_2}$$

while the amino-imino structure presents a second possible type due to resonance in the $C :: N$ group



$$\underset{\substack{::\\ :N:H}}{H_2N : C : OH} \rightleftharpoons \underset{\substack{\cdot\cdot\,\_\\ :N:H\\ \cdot\cdot}}{H_2N : \bar{C} : OH}$$

Finally there is the cyclic structure proposed by Werner which when represented as a zwitterion $\underset{\substack{\cdot\cdot+\\ NH_3}}{HN :: C : \bar{O}}$ can resonate in the same way as the amino-imino structure



$$\underset{\substack{\cdot\cdot+\\ NH_3}}{H : \ddot{N} :: C : \bar{O}} \leftrightharpoons \underset{\substack{\cdot\cdot+\cdot\cdot\\ NH_3}}{H : \ddot{N} : C : \overset{+\,\cdot\cdot\,-}{O} :}$$

TABLE II.

Susceptibility of Resonant Form I.	Susceptibility of Resonant II.	Resultant.
$\underset{\substack{::\\ O:\\ \cdot\cdot}}{H_2N : C : NH_2}$ 27·46	—	27·46
$\underset{\substack{::\\ :N:H}}{H_2N : C : OH}$ 25·75	$\underset{\substack{\cdot\cdot\,\_\\ :N:H\\ \cdot\cdot}}{H_2N : \overset{+}{C} : OH}$ 37·63	31·69
$\underset{\substack{\cdot\cdot+\\ NH_3}}{H : \ddot{N} :: C : \bar{O}}$ 27·90	$\underset{\substack{\cdot\cdot+\cdot\cdot\\ NH_3}}{H : \ddot{N} ::: C : \overset{+\,\cdot\cdot\,-}{O} :}$ 38·80	33·35

The calculated diamagnetic susceptibilities of these structures are given in Table II.

The susceptibility of urea has been determined by three independent workers, Pascal[10] 33·60, Devoto[11] 33·40, Clow 33·66, average 33·56. It will be seen at once that the experimental susceptibility does not support the carbamide structure and that even the amino-imino structure differs from the experimental susceptibility by an amount greater than the experimental error, while the resonating zwitterion agrees with the experimental susceptibility to within the experimental error. Thus there is strong evidence that the parent urea molecule changes its structure on substitution and that in the unsubstituted state it is represented by

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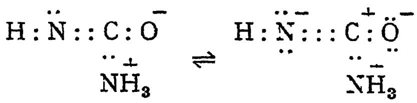
[10] Pascal, *Ann. de Chim.*, 1912, 25, 355.

[11] Devoto, *Rend. Atti Naz. Acad. Lincei*, 1932, 15, 973.



$$H:\ddot{N}::\underset{\overset{..\,+}{NH_3}}{C}:\overset{-}{O} \rightleftharpoons H:\overset{..\,-}{\underset{..}{N}}:::\underset{\overset{..\,-}{NH_3}}{\overset{+}{C}}:\overset{..\,-}{\underset{..}{O}}$$

a resonating zwitterion which is an extension of the cyclic structure originally suggested by Werner.[12] In agreement with this Wyckoff[13] has recently measured the interatomic distances in urea and finds that the $C:NH_2$ distance is 1·37 Å. instead of 1·42 Å and that the distance between C and O is 1·25 Å. which corresponds to neither a single nor a double bond. From these measurements he suggested a resonant structure.

This resonant zwitterion structure is supported by all the purely chemical evidence of Werner as well as by an increasing amount of physical evidence. Table II. shows that none of the non-resonant forms even approaches the experimental susceptibility and that in each case resonance between $C::\ddot{N}:H$ and $\overset{+}{C}:\overset{..\,-}{\underset{..}{N}}:H$ has to be taken into account. This holds throughout the whole of the ureas considered and where a theoretical susceptibility is given in the sequel, excepting the carbamide structure, the value given represents an equal timed resonance between $C::\ddot{N}:H$ and $\overset{+}{C}:\overset{..\,-}{\underset{..}{N}}:H$. The resonance in this group may be the explanation underlying the suggestion by Fearon[14] that the imino and not the amino group is the point of attack of urease on the urea molecule.

(*c*) **Monosubstituted Ureas.**

If urea is a resonating zwitterion while tetra-substituted ureas have a carbamide structure the intervening mono- and di-substituted ureas should show a change in structure, either gradual or abrupt. These intermediate substitution products will now be considered, the experimental susceptibility for the first class being given in Table III. along with the calculated susceptibilities for the various structures.

TABLE III.

	Expt. χ.	Werner.	Amino-imino.	Carbamide.
N-Methyl-urea[15] .	44·62	45·00	43·54	39·24
N-Methylol-urea[16].	48·33	49·65	48·10	43·84
N-Ethyl-urea .	55·50	56·80	55·41	51·10
N-Propyl-urea[10] .	67·40	68·72	67·28	62·96
N-Phenyl-urea .	80·45	82·31	80·87	76·55
O-Methyl-urea[10] .	43·70	—	43·54	—
O-Ethyl-urea[10] .	54·70	—	55·40	—

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[12] Werner, *Chemistry of Urea*, 1923, p. 159.

[13] Wyckoff, *Z. Krist.*, 1934, **89**, 462.

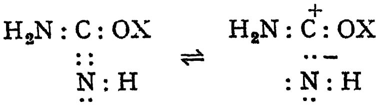
[14] Fearon, *Biochem. J.*, 1936, **30**, 1652.

[15] Pascal, *C.R.*, 1926, 183, 216. The susceptibility 36·72 given in this paper cannot be accounted for by any structure.

[16] Measured in this laboratory by J. M. C. Thompson.

Comparison of the figures given in column 5 with the experimental susceptibilities demonstrates clearly that none of the N-substituted ureas has a substituted carbamide structure. With the exception of N-phenyl-urea the susceptibilities all lie between that of a resonating zwitterion and an amino-imino structure, the equilibrium moving from the zwitterion structure to the amino-imino as one passes from methyl-, ethyl-, to propyl-urea. Substitution of an hydroxy group in the methyl group of N-methyl-urea is almost without influence on the equilibrium, though this may not be generally so. The susceptibility of N-phenyl-urea within the limits of the experimental error suggests a purely amino-imino structure. Werner has already suggested, from chemical evidence alone, that there is an equilibrium between two forms in N-substituted ureas, the equilibrium being nearer a carbamide structure in N-phenyl-urea than in N-methyl-urea. Diamagnetics confirm this, the only difference being that the shift in equilibrium is from a zwitterion to an amino-imino structure instead of from the amino-imino to carbamide.

At this point it is well to consider the structure of O-substituted (iso-) ureas, in which it is known that the substituent group is attached to the oxygen atom. As in the other ureas there will be a resonance



$$\begin{array}{c} H_2N:C:OX \\ :: \\ \underset{..}{N}:H \end{array} \rightleftharpoons \begin{array}{c} H_2N:\overset{+}{C}:OX \\ ..\,- \\ :\underset{..}{N}:H \end{array}$$

but no zwitterion state. The calculated susceptibility is in agreement with experiment (see table), a convincing confirmation of the structure of N- and O-substituted ureas.

	Calc.	Expt.
O-Methyl-urea .	43·54	43·70
O-Ethyl-urea .	55·40	54·70

No other mono-substituted ureas were available for examination, but from these discussed above it will be seen, firstly, that a carbamide structure is never present in a mono-substituted urea; secondly, that all amino-imino structures resonate between $C::\ddot{N}:H$ and $\overset{+}{C}:\underset{..}{\ddot{N}}:\overset{-}{H}$; thirdly, that weighting one end of the molecule causes a shift in the equilibrium from a zwitterion to an amino-imino structure. Finally, substitution in the alkyl group is without effect on the equilibrium.

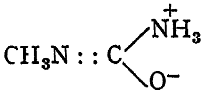
(*d*) **N . N-Disubstituted Ureas.**

The substitution of a second group in urea gives rise to two series of isomeric derivatives depending on whether the two substituent groups are on different nitrogen atoms or not. Consider the latter, the N . N-disubstituted ureas first, where the process of weighting one end of the molecule is continued. The susceptibilities of two of this class are (see table).

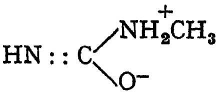
	Expt.	Amino-imino.	Carbamide.
N . N-Dimethyl-urea .	53·62	55·42	51·10
N . N-Diphenyl-urea .	126·30	130·04	125·72

These two results are of the greatest interest, as for the first time a carbamide structure is stabilised. In N . N-dimethyl-urea the equilibrium has passed well beyond the amino-imino structure and the shift is continued in

N . N-diphenyl-urea which is almost wholly N . N-diphenyl-carbamide. Other physical data for N- and N . N-substituted ureas are almost non-existent. It might be noticed, however, that Devoto,[17] from measurements of dielectric constants in aqueous solution, suggests that N-methyl-urea is polar :—


$CH_3N::C\begin{matrix}\diagup \overset{+}{N}H_3\\ \diagdown O^-\end{matrix}$

or


$HN::C\begin{matrix}\diagup \overset{+}{N}H_2CH_3\\ \diagdown O^-\end{matrix}$

while N . N-dimethyl-urea is non-polar, in agreement with the shift in equilibrium deduced from their diamagnetic susceptibilities.

(*e*) Trisubstituted Ureas.

As the carbamide structure is now stabilised further substitution should have little influence on the structure. This is borne out by experiment, Pascal[14] having measured two tri-substituted ureas whose susceptibilities are given in table.

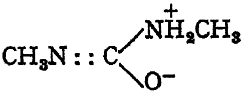
	Expt.	Carbamide.
N . N-Diethyl-N′-phenyl-urea .	126·39	126·99
N . N-N′-Triphenyl-urea .	176·46	174·89

(*f*) N . N′-Disubstituted Ureas.

The only group remaining to be discussed is the N . N′-disubstituted ureas. Four ureas in this group have been measured, but the results of the various experimenters are not in as good agreement as might be desired.

	Clow.	Devoto.[10]	Pascal.[14]	Amino-imino.
N . N′-Dimethyl-urea .	60·03	56·30	—	56·49
N . N′-Dimethylol-urea .	68·00	—	—	64·52
N . N′-Diphenyl-urea .	127·6	—	132·7	130·04
N-Methyl-N′-phenyl-urea .	—	—	93·35	92·73

In general the results indicate amino-imino structures, with the exception of N . N′-dimethylol-urea. This urea was subjected to repeated measurements, but its susceptibility remained at a value which implied a resonating zwitterion. Further work will be necessary before a conclusive statement can be made about these ureas. As far as can be seen at present the N . N′-disubstituted ureas revert to the type of structure characteristic of mono-substituted ureas. Devoto gives


$CH_3N::C\begin{matrix}\diagup \overset{+}{N}H_2CH_3\\ \diagdown O^-\end{matrix}$

as the structure of the symmetrical di-methyl derivative. These changes are qualitatively the same as those found by de Beer, Buck and Hjort for the anæsthetic effect of ureas for which the anæsthetic effects decrease in the following order: N-alkyl, N . N′-dialkyl, N . N-dialkyl, N . N-N′-trialkyl-ureas, the same order as that in which they pass from the zwitterion to the carbamide structure. They also observed that N . N′-dialkyl-ureas containing an ethyl group had a smaller anæsthetic effect than the other N . N′-disubstituted ureas, indicating a carbamide structure. This has been confirmed, N . N′-diethyl-urea having a susceptibility 74·07, the calculated value for a carbamide structure being 74·82. The reason for this variation in ureas containing an ethyl group has not been explained.

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[17] Devoto, *Gazz. chim. ital.*, 1932, **61**, 897.

Summary.

The possible resonance structures of urea and eighteen of its derivatives has been investigated by a discussion of their diamagnetic susceptibilities, following the method of Gray and Cruickshank (*Trans. Faraday Soc.*, 1935, **31**, 1491), which reveals a change in the parent molecule from a resonating zwitterion in urea itself through an amino-imino structure in N-mono-substituted ureas to carbamide in a tetra-substituted molecule. When there is a C : : N group in the molecule this is shown to resonate between $C::\overset{\cdot\cdot}{N}:$ and $\overset{+}{C}:\underset{\cdot\cdot}{\overset{\cdot\cdot\,-}{N}}:$.

The author wishes to express his gratitude to Dr. Francis W. Gray, who was prevented from being a co-author by illness, for his continued interest in the work both in the experimental stages and afterwards.

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THE ELECTRONIC STRUCTURE OF METHANE.

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Communicated by Professor J. E. Lennard-Jones, F.R.S.

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A complete study of the methane molecule is essential to any real understanding of all organic chemistry, since it is the simplest molecule to exhibit the characteristic tetrahedral valence of Carbon. Van Vleck [1] in a very careful investigation, has shown that both the electron-pair methods of Heitler, London, Pauling, and Slater, as well as the molecular-orbital methods of Hund, Lennard-Jones and Mulliken, agree in predicting a tetrahedral model for CH_4, and it is reasonable to interpolate between these two theories, and believe that a fuller treatment, which would be intermediate between the two, would also predict such a model. When we discuss the energies, however, the position is not so satisfactory. It is true that Woods [2] using electron-pair methods, obtained good numerical agreement, but, as Van Vleck shows, this must be regarded as fortuitous, since the hybridisation postulated is not perfect and the effect of electronic screening due to the four H atoms was not allowed for. More recently, Voge[3] has shown that the effect of resonance with other states, not allowed for by Woods, increases the stability of the molecule by about 1·2 volts. This resonance also has the effect of lowering the energy of the "valence-state" (the excited state discussed by Van Vleck comprising such combinations of the six sp^3 levels as will give four strong bonds for the C atom) by 2·5 volts, making it about 4·5 volts higher than the divalent ground state $s^2p^2\,{}^3P$, instead of 7 volts as Van Vleck first calculated it. In view of the difficulties of these methods and the fact that even such numerical results as have been obtained (with the solitary exception of Woods' work) have been obtained by the use of reasonably-likely values for most of the integrals concerned (a situation not very satisfactory to the theoretician) it has seemed worth while to investigate the electronic structure of the molecule numerically, from an aspect not discussed in the work of Woods and Voge and only treated in a qualitative way by Van Vleck. The method of molecular orbitals has therefore been applied to a study of the ground state and some of the excited states of this molecule.

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[1] Van Vleck, *J. Chem. Physics*, 1933, **1**, 177, 219; 1934, **2**, 20.
[2] Woods, *Trans. Faraday Soc.*, 1932, **28**, 877.

The present treatment can only be regarded as tentative; but the complete solution of the problem must proceed in stages and in this paper the complexity of the situation and the various obstacles in the way of such a complete solution become more evident. Furthermore, before a complete solution is attempted, it is desirable that the problem should be discussed from as many different angles as possible, so that the effects of different simplifying assumptions may be clearly understood.

There are, in addition, various other calculations, such as the effects of applied electric and magnetic fields, and the scattering of electrons, for which explicit, even though approximate, knowledge of the wave-functions for the individual electrons, is essential, and this provides an extra justification for the present line of approach.

The Method of Molecular Orbitals.

There are two problems essential to any discussion of methane—the nuclear pattern and the electronic energies. The first of these has been adequately treated (to our present degree of approximation) by Van Vleck,[1] and we can assume that the C nucleus is at the centre, and the H nuclei (1, 2, 3, 4) at the corners, of a regular tetrahedron. It is convenient to draw the circumscribing cube and to assume that the axes of x, y and z bisect the six faces, as shown in Fig. 1. There are ten electrons

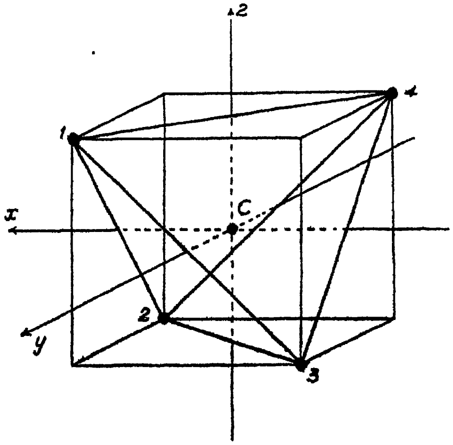

FIG. 1.

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[3] Voge, *J. Chem. Physics*, 1936, 4, 581.

to be housed in this nuclear framework, and, as in the case of diatomic molecules,[4] we imagine them fed, one at a time, into the " orbitals," allowing not more than two to each cell. The various orbitals have been discussed from symmetry considerations, by Mulliken[5] and others; we need only consider the two types " *a* " and " *t*." Of these, " *a* " has the greatest symmetry possible, being almost spherically symmetrical and " *t*," triply degenerate, resembles most closely a *p*-wave-function directed along either of the three axes of co-ordinates. In the ground state $^1A_1$ the lowest two " *a* " orbitals and the three equivalent " *t* " orbitals are all filled, thus completing a molecular shell and assuring great stability with respect to electron addition, and also an almost spherical charge distribution.

There are some more approximations to make; although in a fuller treatment, more appropriate descriptions would have to be found, we shall use the LCAO expansion of each molecular orbital, as discussed by Mulliken,[6] where LCAO is short for " linear combinations of atomic orbitals." The atomic orbitals themselves, however, will be allowed a certain amount of flexibility by the use of variable exponents, and a variational method is used to obtain the lowest possible energy. The calculations will also only be made at the equilibrium distance

$$\text{C—H} = 2{\cdot}0 \text{ a.u.}$$

We shall use atomic units (a.u.) throughout.

The Orbitals.

We assume that the four different molecular orbitals are built up out of linear combinations of the four H-atomic orbitals $\psi(H_r)$ where $r = 1, 2, 3, 4$ and the 1*s*. 2*s* and 2*p* orbitals of carbon:

$$\psi(C:1s),\ \psi(C:2s),\ \psi(C:2p_x),\ \psi(C:2p_y) \text{ and } \psi(C:2p_z).$$

Then, as Van Vleck and Sherman[7] have shown, we may group these nine orbitals into combining and non-combining groups, such that only members of the same group combine in the LCAO approximation.

" *a* " group $\psi(C:1s),\ \psi(C:2s),\ \{\psi(H_1) + \psi(H_2) + \psi(H_3) + \psi(H_4)\}$,

" t_x " group $\psi(C:2p_x),\ \{\psi(H_1) + \psi(H_2) - \psi(H_3) - \psi(H_4)\}$.

The groups t_y and t_z are obtained from t_x by obvious permutations. The expressions in braces { } may be thought of as composite orbitals, relating to the structure H_4, which are composed entirely from wave-functions around the four protons, and whose form is dictated by the symmetry of the nuclear framework. These composite orbitals are of some importance when we consider the polarity of the complete orbitals toward the end of the paper.

The lowest of all the " *a* " orbitals will be practically equivalent to the K-orbitals of atomic carbon. A more complete approximation would be:—

$$\psi = \lambda\,\psi(C:1s) + \mu\{\psi(H_1) + \psi(H_2) + \psi(H_3) + \psi(H_4)\} + \nu\,\psi(C:2s)$$

but the ratios μ/λ and ν/λ will be so small, due to the large energy difference between $\psi(C:1s)$ and either $\psi(H)$ or $\psi(C:2s)$ that we may put $\mu/\lambda = \nu/\lambda = 0$ without serious loss. The actual form of $\psi(C:1s)$ may, to our degree of approximation, be taken to be that of Slater[8]—$\psi(C:1s) = e^{-\gamma r}$ with $\gamma = 5{\cdot}6875$ and r is measured from the C nucleus, $r_1\ r_2\ r_3\ r_4$ from the H nuclei in order. This simple form for the lowest orbital does not allow for the perturbation caused by the presence either of the four protons or of the other eight electrons. We can show, however, that this perturbation is extremely small, so small that it may safely be neglected. Its order of magnitude may be obtained by considering the effect upon the energy, caused by the Coulomb forces due to the four protons; these give rise to a perturbing potential:

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[4] Lennard-Jones, *Trans. Faraday Soc.*, 1929, **25**, 668.

[5] Mulliken, *J. Chem. Physics*, 1933, **1**, 492.

[6] *Ibid.*, 1935, **3**, 375.

[7] Van Vleck and Sherman, *Rev. Mod. Physics*, 1935, **7**, 167.

$$V_{\text{pert}} = 1/r_1 + 1/r_2 + 1/r_3 + 1/r_4.$$

V_{pert} may be expanded as a series of Legendre's Polynomials around the origin, and it appears that each of the two K-electrons suffers a perturbation with energy change:

$$E_{\text{pert}} = -4/\rho + 8(1 + \gamma\rho)\,.\,e^{-\frac{2\gamma\rho}{\rho}}.$$

If the K-electrons were each concentrated at the origin (thus effectively cancelling $+2e$ of the central charge on the carbon nucleus) we should expect a perturbation energy $4 \times -1/\rho$ since the negative charge is at a distance ρ from each of four separate unit positive charges. So the second half of E_{pert} is a measure of the distortion due to the four protons, and since $\gamma\rho = 11{\cdot}4$ it is entirely negligible. We may thus say that the C nucleus + K-shell behaves exactly like a nuclear charge of + 4 units; there is, however, one other point to be remembered—that the wave-functions for the other orbitals of symmetry "*a*" must be orthogonal to the atomic wave-function $e^{-\gamma r}$. No restriction is placed upon the *t*-orbitals since they are of different symmetry and are therefore automatically orthogonal to every *a*-orbital.

The second "*a*" orbital will be expressed as:

$$\psi(2sa) = \lambda\,\psi(C:2s) + \mu\{\psi(H_1) + \psi(H_2) + \psi(H_3) + \psi(H_4)\}.$$

The ratio of the coefficients λ, μ will have to be determined by a variation method, as well as any other parameters that may occur in $\psi(H)$ and $\psi(C:2s)$. There will be two solutions[9] of the variational equation in λ and μ, and provided that the atomic energies corresponding to $\psi(C:2s)$ and $\psi(H)$ are approximately equal (as, indeed they are), and provided also that other possible atomic states that we might add to the wave-function are considerably higher up the energy scale (as, in fact, they are), then these two solutions will be fairly good approximations to the next two "*a*" orbitals. Following Mulliken's terminology, let us write the two orbitals [*s*] and [*s**] and suppose that [*s*] has the lower energy. Exactly similar considerations apply to each "*t*" orbital, whose form is:

$$\psi(2t_x) = \lambda\,\psi(C:2p_x) + \mu\{\psi(H_1) + \psi(H_2) - \psi(H_3) - \psi(H_4)\}$$

and which gives rise to [*p*] and [*p**].

The Hamiltonian and Effective Nuclear Charges.

The complete Hamiltonian for the molecule will involve Coulomb terms from the five nuclei and electron-repulsion terms. It is evidently impossible to solve the ten-electron problem, and we have to approximate by supposing that each electron moves in an effective field which has more or less " smoothed out " the electron repulsions. This effective field for the K electrons of carbon will, as we have shown, be merely the atomic field; the effective fields for the bonding [s] and [p] electrons will probably differ slightly from one another, but considerations of computation have made it desirable to assume that all the eight bonding electrons move in the same effective field, which we suppose to be represented by a positive charge Z_c on the carbon nucleus and Z_h on each hydrogen nucleus. So the Hamiltonian, which could not be separated in its original form, now becomes separable, corresponding to eight non-interacting electrons, and may be written :

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[8] Slater, *Physic. Rev.*, 1930, 36, 57.

[9] Coulson, *Proc. Camb. Phil. Soc.*, 1936, 32.

$$H = H_s(1) \quad + H_s(2) + H_p(3) + H_p(4) \; . \; . \; . + H_p(8)$$

where :

$$H_s = H_p = -\tfrac{1}{2}\nabla^2 - Z_c/r - Z_h\,(1/r_1 + 1/r_2 + 1/r_3 + 1/r_4)$$

and the suffix denotes that the corresponding wave-function is of type [s] or [p]. With such Hamiltonians the wave-function for the eight bonding electrons becomes just a product of individual orbital functions, or, if we prefer, a determinant of eight rows and columns ; but in either case, since the wave-functions are all orthogonal, the total electronic energy is merely the sum of the various single-electron energies, and we may write :

$$E = 2 \, . \, E_s + 6 \, . \, E_p$$

if we are dealing with the ground state and are concerning ourselves only with the eight bonding electrons. This is not quite the usual Hartree self-consistent-field method, since, as Coolidge has pointed out, it is almost equivalent to counting the Coulomb charge-cloud repulsions twice over. But any other method would be much too complicated.

Concerning the values of Z_c and Z_h which occur in the Hamiltonian above, little can be said with definiteness. But there are good reasons for supposing that Z_h is rather less than unity. For if there were no screening at all, then Z_h would be unity ; however, screening from the other electrons will tend to reduce this and complete atomic screening [8] reduces Z_h by 5/16. The reduction will be less than this in our case since the screening is supplied by electrons which are not " full-time " on the H-nuclei, and the approximate value $Z_h = 0{\cdot}9$ seems a fair estimate. The numerical work that follows will be devoted to finding a value for Z_c which satisfies the observed energy conditions and then using this value to predict some of the critical potentials. The final value for Z_c (we shall show that it is about 1·72) would be somewhat altered if Z_h varied from 0·9. There is no satisfactory way yet of obtaining both the effective charges simultaneously, and in any case the LCAO Hartree method is only an approximation, so that Z_h has been given the uniform value of 0·9 and calculations have been performed with a series of values for Z_c.

The Wave-functions.

The following forms were used for the wave-functions :

$$\psi(\mathrm{C} : 2s) = \sqrt{\frac{\alpha_s^5}{3\pi}} \, . \, re^{-\alpha_s r},$$

$$\psi(\mathrm{H}_1) = \sqrt{\frac{\beta^3}{\pi}} \, e^{-\beta r_1},$$

$$\psi(\mathrm{C} : 2p_x) = \sqrt{\frac{\alpha_p^5}{\pi}} \, r \cos \theta_x \, e^{-\alpha_p r}.$$

For the $[s]$ orbitals we have to vary the parameters α_s, β and λ/μ and for the $[p]$ orbitals α_p, β and λ/μ to find the minimum energy. Another simplification was here introduced—β was put equal to 1. The reasons for this are quite simple; first of all· its precise value does not greatly alter the energy values (a result long known in atomic calculations) and secondly we expect, by analogy with H_2, that β/Z_h would be about 1·15 which was the value found in some unpublished work of the writer. With Z_h put equal to 0·9 this would make β about equal to 1·035. The value $\beta = 1$ simplifies the calculations considerably.

It may be argued that although the $[p]$ orbital is satisfactory, the $[s]$ orbital does not satisfy the conditions which it should satisfy if we are to use a variational method, of being orthogonal to the wave-function of the K-electron. But, in fact, it almost does, since the integral $\int \psi(\mathrm{C} : 1s) \,.\, \psi[s] \, d\tau$ is very small and the resultant "sagging" of the energy value is not very appreciable. As a check the more complicated wave-function

$$\psi(\mathrm{C} : 2s) = (r - b) \,.\, e^{-\alpha_s r}$$

was used and the energies evaluated when b was chosen as a function of α_s so that $\psi(\mathrm{C} : 2s)$ was orthogonal to $\psi(\mathrm{C} : 1s)$. The value of b was small, (between 0·4 and 0·5) and the energies corresponding to the new function did not differ greatly from those obtained with $\psi(\mathrm{C} : 2s) = r \,.\, e^{-\alpha_s r}$. It is interesting to note that Slater [8] who neglects the nodes in r in his atomic calculations, finds almost the same energy values as Zener [10] who includes them. We have therefore kept throughout to the simpler wave-function.

The Calculations.

Both the $[s]$ and $[p]$ orbitals were evaluated with Z_c equal to 1·0; 1·2; 1·4; 1·6; 1·8 and 2·0. The minimising with respect to the exponents α_s and α_p had to be done graphically; but the result is quite accurate since it transpired that a considerable change in α made little change in the energy. The variation of the parameter λ/μ was achieved just as with a diatomic molecule, as in [9] except that the two component wave-functions are, for the $[s]$ orbital: $\psi(\mathrm{C} : 2s)$ and the composite function

$$\{\psi(\mathrm{H}_1) + \psi(\mathrm{H}_2) + \psi(\mathrm{H}_3) + \psi(\mathrm{H}_4)\},$$

and for the $[p_x]$ orbital: $\psi(2p_x)$ and the composite function

$$\{\psi(\mathrm{H}_1) + \psi(\mathrm{H}_2) - \psi(\mathrm{H}_3) - \psi(\mathrm{H}_4)\}.$$

A word should be included concerning the evaluation of the various integrals; since we have smoothed-out all the r_{12} terms, the only integrals that can occur will contain the co-ordinates of just one electron. They may involve distances from one or two nuclei, as, for example, $\int \frac{1}{r_1} e^{-\alpha r - \beta r_1} d\tau$ in which case they can all be evaluated quite easily in the manner suggested by Lennard-Jones [4] by transforming to spheroidal co-ordinates with those two nuclei as foci, or they may involve distances from three nuclei, as for example, $\int \frac{1}{r_2} e^{-\alpha r - \beta r_1} d\tau$ in which case, their calculation is very obstinate and was performed by the use of a method developed by the writer.[9]

[10] Zener, *Physic. Rev.*, 1930, 36, 51.

Results.

The variation with respect to α was performed separately for each of the six chosen values of Z_c, and the resulting curves, showing the energies of [s] [s*] [p] [p*] as functions of Z_c, are given in Fig. 2. In Fig. 3 are shown the corresponding values of λ/μ. Attention is directed to the fact that since each individual ψ is normalised to unity, the composite orbital

$$\{\psi(H_1)+\psi(H_2)+\psi(H_3)+\psi(H_4)\}$$

is not so normalised, and in fact $\int\{\psi(H_1)+\psi(H_2)+\psi(H_3)+\psi(H_4)\}^2 d\tau = 4 + 12 . \int\psi(H_1) . \psi(H_2)\ d\tau = 7{\cdot}582$ and $\int\{\psi(H_1)+\psi(H_2)-\psi(H_3)-\psi(H_4)\}^2 d\tau = 4-4 . \int\psi(H_1) . \psi(H_2) . d\tau = 2{\cdot}806$.

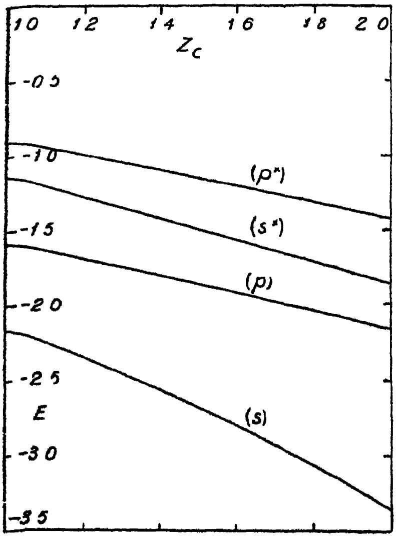

FIG. 2.

One immediate conclusion from Fig. 2 is that the [p] orbital is less bonding than the [s]. This confirms the result of Mulliken, obtained empirically. We have already shown that with this analysis, the total energy of the eight bonding electrons is to be taken as $2 . E_s + 6 . E^c$. The variation of this quantity with Z_c is shown in Table I. To get the binding energy of the molecule, we must subtract the nuclear repulsions, in this case 9·84 a.u., the energy of the four hydrogen atoms (2·0 a.u.) and the energy of the *L*-shell of carbon. This latter depends, as

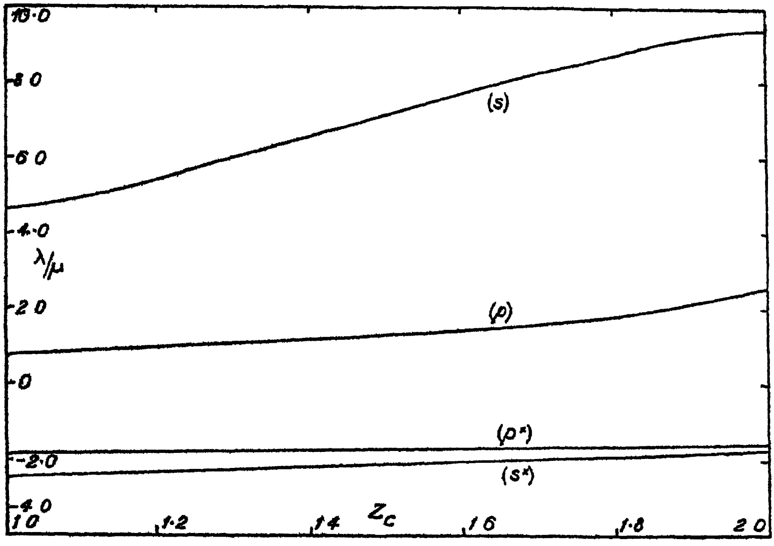

FIG. 3.

TABLE I—ENERGY OF CH_4 AS A FUNCTION OF NUCLEAR CHARGE Z_c.

Z_c	1·0	1·2	1·4	1·6	1·8	2·0
E_s	2·159	2·353	2·568	2·803	3·064	3·351
E_p . . .	1·582	1·687	1·796	1·912	2·032	2·160
$2 . E_s + 6 \ E_p$.	13·810	14·828	15·912	17·078	18·320	19·662
Binding energy of molecule (a u) .	−3·31	−2·29	−1·21	−0·04	+1·20	2·54
Binding energy per bond (a u.) . .	−0·83	−0·57	−0·302	−0·010	0·300	0·635
Binding energy per bond (volts) .	−22·5	−15·5	−8·2	−0·27	8·14	17·2

Slater energy for the L-shell of carbon = 5·28
Energy of C + 4 . H (less carbon K-shell) = 7·28
Nuclear repulsions when $\rho = 2{\cdot}0$ = 9·84

we have discussed earlier, on whether we take the divalent ground level s^2p^2 or the "valence-combination" of the sp^3 states Let us take the former as our standard. The energy of the L-electrons, which for greatest accuracy should be computed by a method as nearly as possible parallel to that used for the molecule, is, according to Slater — 5·28 a.u. (The true value is — 5·317 a.u. so that not much error is introduced here). With this data the binding energy of the molecule, regarded as the energy required to split up a molecule of CH_4 into a divalent C atom and four isolated H atoms, is obtained, and hence also the energy per bond. This value is shown in the last line of the table and also graphically in Fig. 4. This last curve enables a sharp choice of Z_c to be made; for the experimental value of the bond energy is about five volts, and we conclude that $Z_c = 1{\cdot}72$ gives the correct energy. Reference to Figs. 2 and 3 now enables the two states to be described thus:

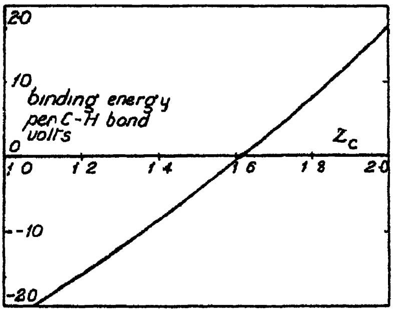

FIG. 4.

$$[s] \quad E_s = -\,2{\cdot}96 \qquad \alpha_s = 2{\cdot}98 \qquad \lambda/\mu = 8{\cdot}22.$$
$$[p] \quad E_p = -\,1{\cdot}984 \qquad \alpha_p = 1{\cdot}620 \qquad \lambda/\mu = 1{\cdot}70.$$

If the same nuclear charges apply to the excited states, these will be given by:

$$[s^*] \quad E_s = -\,1{\cdot}70 \qquad \alpha_s = 3{\cdot}18 \qquad \lambda/\mu = -\,1{\cdot}952$$
$$[p^*] \quad E_p = -\,1{\cdot}268 \qquad \alpha_p = 1{\cdot}125 \qquad \lambda/\mu = -\,1{\cdot}640.$$

The value of Z_c which we have now obtained is quite a reasonable one, if we think of it as an average over the s and p electrons. Penney[11] in discussing Bartlett's theory of C($2p$) binding in relation to the C=C bond, says that "to put Z equal to 2·5 for this kind of binding is rather high."

Vertical Ionisation.

We can now discuss what Mulliken calls the "vertical ionisation." This is the energy required to eject an [s] or [p] electron without changing nuclear dimensions. At first sight it looks as though the values should be 2·96 and 1·984 a.u., *i.e.* 80·1 and 53·7 volts. These values are obviously incorrect, since Mulliken[12] estimates 22 volts for [*s*] and the observed value for [*p*] is 14·4 volts. However the ratio 80·1/53·7 (= 1·50) is almost the same as Mulliken's ratio 22/14·4 (= 1·53). The discrepancy has arisen because our value of 53·7 volts for the removal of a [*p*] electron is the mean value obtained if the electrons are all independent; but in actual fact the removal of one of the six equivalent [*p*] electrons will cause an alteration in the screening constants and quite a large rearrangement in the other electrons which are left, and we shall recover in this reorganisation a good deal of the energy required to eject the original electron. As a consequence, more and more energy is needed for successive removals of [*p*] electrons, a situation which would only become clear in our numerical work if we were able to evaluate the energies of CH_4^+, CH_4^{++}, etc. Failing such analysis, our best course is to assume that the successive ionisation energies vary in much the same way in a molecule as in an atom. The first ionisation potentials for the series of atoms C, N, O, F and Ne are known experimentally[13] and are shown in Table II. The mean ionisation energy for all the *L*-electrons present in each case can be found if the total energy of the *L*-electrons is known; and the rules of Slater[8] yield values for this quantity accurate to 2 per cent. In the cases of C, N and O, where experimental values can be obtained, or guessed satisfactorily, the values are shown in the table and may be compared with the Slater values; the error is not very large. There is no reason why this error should be appreciably greater in the cases of F and Ne, where experimental values are not known. Thus the number *k*, defined as the ratio of the first ionisation energy to the mean ionisation energy of the *L*-electrons present, is obtained. In estimating the value of *k*, it is far better to use the experimental value for the first ionisation energy, since the Slater value, shown in the table for comparison, is quite inaccurate for the later members of the series. Thus the true ionisation energy can be found from the mean ionisation energy if we multiply by this ratio *k*, which varies regularly from 0·314 for carbon to 0·185 for Ne. We have to consider which of these five atoms, the molecule CH_4 most nearly resembles. Conceptually, the electronic orbitals are related to those of Ne when the molecule contracts in size and to those of C when the molecule expands. But the energy values of each orbital (and it is with energy values and differences that we are concerned at the moment)

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[11] Penney, *Proc. Physic. Soc.*, 1934, 46, 333.

TABLE II.—Atomic Ionisation Potentials.

Atom.	First Ionisation Potential.		Mean Ionisation Potential for *L*-Electrons.		*k*.
	Theor.	Expt.	Theor.	Expt.	
C .	·421	·418	1·320	1·329	·314
N .	·475	·535	1·931	1·936	·277
O .	·521	·501	2·588	2·628	·191
F .	·558	·624	3·380	—	·185
Ne .	·58	·794	4·28	—	·185

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[12] Mulliken, *J. Chem. Physics*, 1935, 3, 517.

[13] Noyes and Beckman, *Chem. Rev.*, 1928, 5, 85.

are much nearer to those of C than of Ne. This is due to the fact that the energy of an orbital is proportional to Z^2 and a " diffuse " central charge, divided between the C nucleus and the four protons will cause a much smaller energy value than if the charge was all concentrated at one spot. We may therefore expect that the ratio k will have a value rather nearer to the value for C than for Ne. The mean of these two values is 0·250 and we shall accordingly assume that for CH_4, $k = 0{\cdot}27$, though the true value may lie anywhere between 0·31 and 0·23. Using this value for k, and its possible error, the vertical ionisation for the molecule are soon obtained ; they are shown in Table III. It is unfortunate that a factor of this kind should have to be introduced, since it provides a measure of uncertainty in the final values ; however, there seems no reasonable way of avoiding it. The final figures, of course, are quite as good as one would have anticipated from this type of treatment.

TABLE III.—VERTICAL IONISATION (VOLTS).

	Present Paper.	Mulliken.
[*s*] .	21·6 ± 3·0	22·0
[*p*] .	14·5 ± 2·0	14·4

Excitation.

The ground level is $[s]^2\,[p]^6\,{}^1A_1$ and there are two excited levels which we may write $[s]^2\,[p]^5\,[s^*]\ {}^{1,\,3}T_2$ and $[s]\,[p]^6\,[p^*]$. Of these the former is clearly the one with the least energy of excitation. If the orbitals for the excited molecules have the same effective nuclear charges as those for the ground level, the transition ${}^1A_1 - {}^1T_2$ has an energy equal to $1{\cdot}98 - 1{\cdot}70 = 0{\cdot}28$ a.u. or 7·6 volts. This agrees pretty well with the observed value[12] of 9·9 volts. The other excitation potential would be $2{\cdot}96 - 1{\cdot}27 = 1{\cdot}69$ a.u. $= 46$ volts which is in the range of the continuous spectrum ; no experimental evidence is available to check this. The calculated value of 7·6 volts for the observed transition should be somewhat modified, in a manner similar to that used in the preceding paragraph for the ionisation energies. But the modification, which would tend to reduce the figure slightly, will be much less drastic than with ionisation, since when the molecule changes from the ground level to the first excited state, the change in screening constants will be decidedly less than if the excited electron were completely removed.

Polarity.

Reference to the wave-functions shows that for the [*s*] orbital λ/μ is 8·22 and for the [*p*] orbital 1·70. If, instead of using the normalised atomic functions $\psi(H)$, we had normalised the non-localised orbitals

$$\{\psi(H_1) + \psi(H_2) + \psi(H_3) + \psi(H_4)\}$$

and

$$\{\psi(H_1) + \psi(H_2) - \psi(H_3) - \psi(H_4)\},$$

then these ratios become 1·08 and 0·61 respectively. This would indicate that the [*s*] orbital is almost homopolar with a slight preponderance of charge on the C nucleus, and that the [*p*] orbital is definitely the other way, with the charge-cloud shifted on to the H nuclei. This is in only partial agreement with Mulliken[14] who concludes that the [*s*] orbital should be strongly polar with the charge on the C nucleus and the [*p*] orbital only slightly polar the other way. A partial reconciliation is possible if the nuclear charges are allowed to differ for the [*s*] and [*p*] orbitals, since this would tend to increase Z_c for the [*s*] and thus throw more charge on to the C atom. A possible error may have crept into Mulliken's work, since the non-localised orbitals for the H_4 group, do differ in energy from the orbitals of a simple H atom, and hence presumably also in electroaffinity, an effect which in this case will tend to decrease the net charge on the C atom. This point is worth a fuller investigation.

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[14] Mulliken, *J. Chem. Physics*, 1935, 3, 586.

The last point which we shall mention in this account is connected with two predictions of Mulliken[15] concerning electroaffinities. The first is that in most cases of nearly homopolar binding,* $S^2 = 0{\cdot}42$, where S is the overlap[9] integral $\int\psi_a\psi_b\,d\tau$. The second * is that the function which he calls Y, and which is equal to $H_{ab} - \frac{1}{2} S_{ab}(H_{aa}+H_{bb})$ is nearly constant from molecule to molecule. In this notation, ψ_a and ψ_b are the two components of the LCAO approximation, and H_{ab} is the matrix component of the Hamiltonian with respect to these two functions: $\int\psi_a\,.\,H\,.\,\psi_b\,.\,d\tau$. Concerning the value of this constant, Mulliken says that " $-$ 1·72 volts is probably far too small." In our cases we find that for the [*s*] orbital, $S^2 = 0{\cdot}232$ and for the [*p*] orbital $S^2 = 0{\cdot}426$. Also, that Y is certainly negative with the values $-$ 11·6 volts for [*s*] and $-$ 7·02 volts for [*p*]. The fact that Y for [*s*] is numerically greater than Y for [*p*] agrees with Mulliken † who writes: " It appears likely, however, that Y may be larger for the [*s*] than for the [*p*] orbitals."

In conclusion, the writer wishes to thank Professor J. E. Lennard-Jones, F.R.S., for suggesting this problem and for his continued help, and the Department of Scientific and Industrial Research for a grant.

Summary.

The method of molecular orbitals is applied to a preliminary study of the ground state and some excited levels of CH_4. With a suitable scheme of effective nuclear charges (0·9*e* on each H nucleus and 1·72*e* on the carbon nucleus) the correct binding energy is obtained, and these values give quite fair agreement with those critical potentials that have been determined. A discussion is given of the polarity of the orbitals, and explicit forms are obtained for the wave-functions of the various orbitals.

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[15] Mulliken, *J. Chem. Physics*, 1935, 3, 573.

* See [15] p. 583. † See [15] p. 589.

STUDIES IN MEMBRANE PERMEABILITY.
I. THE MEASUREMENT OF THE PERMEABILITY OF MEMBRANES TO SOLUTES.

By E. J. Hartung, F. H. C. Kelly and J. Wertheim.

Received 16*th November*, 1936.

The extensive researches of L. Michaelis and collaborators[1] on the conductivity, permeability and potential of the dried collodion membrane have placed the theory of the action of this membrane on a sound basis. In their papers much experimental and theoretical evidence is adduced to prove that with uni-univalent electrolytes as solutes the membrane potential depends on differential diffusion rates of kation and anion in the membrane, which rates in turn are influenced by the adsorption of one or other ion (here preferentially the anion) on the walls of the pores. With larger ions and non-electrolytes the membrane behaves more like a sieve with sets of pores of various diameters, and the availability of these pores for diffusion depends on the size of the diffusing entities. Despite great care in preparation, dried collodion membranes were found to differ considerably in properties from one another, and in all cases the permeability to solvent and solutes was very low indeed, so that refined methods were necessary to detect and measure it quantitatively. If the views of Michaelis can be applied generally, some kind of inverse relation should exist between the rate of penetration of a solute and the degree of its adsorption by the membrane substance, at least for electrolytes of similar ionic diameter. This does not appear to have been tested for dried collodion, which indeed is not well suited to the investigation because of its very low permeability and relatively small surface. One of us [2] had previously examined the adsorption of KCl and K_2SO_4 on cupric ferrocyanide; accepting the results of Tammann [3] and later workers that the chloride penetrates this membrane more readily than the sulphate, these experiments support qualitatively the theory of Michaelis, for K_2SO_4 is more strongly adsorbed by cupric ferrocyanide than KCl.

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[1] L. Michaelis and W. A. Perlzweig, *J. Gen. Physiol.*, 1927, 10, 575, and succeeding papers.

We are at present making a thorough study of the permeability and adsorbing powers of cupric ferrocyanide, which has the advantage of much greater permeability to solvent and solute than dried collodion; it also lends itself well to adsorption work because of the very large surface of the precipitated substance. Its disadvantages are its complex composition, which varies with the mode of formation, and its extreme frailty, which necessitates some kind of support for the membrane made from it. Tammann's early experiments on permeability were made with the unsupported membrane formed between the superposed membranogen solutions, to one of which the solute to be tested was added. This method was qualitative only, and the presence of the membranogens led to much confusion in the interpretation of the results owing to the possibility of ionic exchange across the membrane. The unsupported membrane is otherwise ideal because of its thinness, but our attempts to use it quantitatively after removal of the membranogens have so far failed because of its excessive liability to rupture. Walden [4] introduced the use of hardened gelatine in which the cupric ferrocyanide was precipitated, and Tammann [5] suggested parchment for this purpose. These materials, or toughened filter paper, have usually been used in subsequent work, *e.g.* H. B. Weiser,[6] R. Collander.[7] Unglazed porcelain, used by Bartell,[8] is less suitable owing to its thickness.

We have been unable to find in the literature satisfactory quantitative measurements of the rate of penetration of a membrane by solutes. The usual procedure has been to impregnate a suitable parchment or other thimble with the membrane substance,[6] or to close the lower end of a wide glass tube with gelatine [7] in which the membrane substance is afterwards precipitated. Much work has also been done with thin collodion membranes rendered suitably porous by previous treatment and used in the form of thimbles, or flat sheets closing one end of a glass tube or clamped between glass rings. In the vessels so formed the solution to be investigated is placed, and the apparatus is dipped into distilled water (or other solvent in use). After a suitable interval, usually several hours and often days, the solute which has diffused into the solvent outside is determined quantitatively. Membranogens are sometimes maintained in solution on either side of the membrane, and sometimes not; often no special precautions against temperature changes are taken. In order to diminish osmotic exchange of solvent, diffusion is sometimes permitted into an isotonic solution of supposedly inert solute, *e.g.* sucrose.

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[2] E. J. Hartung, *Trans. Faraday Soc.*, 1920, **15**, (3), 170.

[3] G. Tammann, *Wied. Ann.*, 1888, **34**, 299.

[4] P. Walden, *Z. physik. Chem.*, 1892, **10**, 699.

[5] G. Tammann, *ibid.*, 1892, **10**, 255.

[6] H. B. Weiser, *J. Physic. Chem.*, 1930, **34**, 335.

[7] R. Collander, *Kolloidchem. Beihefte*, 1924, **19**, 72; C. Gurchot, *J. Physic Chem.*, 1926, **30**, 83.

[8] F. E. Bartell, 1912, **16**, 318.

The main objection to this general procedure lies in the uncertainty and variability of the concentration gradient. During the experiment the concentration of the inner solution steadily decreases and that of the outer solution increases. Consequently, two solutes of differing penetration are not compared under similar conditions, even though initial concentrations of solutions and total time of diffusion are similar, for the respective rates of alteration of the gradient across the membrane are not the same at corresponding times. Moreover, with the thimble type of membrane the concentration gradient of a single solute at any instant is not the same all over the membrane, since the diffused solute sinks down over the outer surface of the thimble and pours away from its lower end owing to the increasing density of its solution. The osmotic exchange of solvent across the membrane is therefore also variable; this exchange is always present, makes knowledge of the actual concentration gradient still more vague and interferes with the interpretation of the results. Its effect may be diminished, but obviously not prevented, by making the external solution at the start of the experiment isotonic with the inner solution by means of a non-penetrating solute. If electrolytes are present on both sides of the membrane (*e.g.* as membranogens in part) the problem of concentration gradient may be further complicated by the tendency to attain a Donnan equilibrium. These general criticisms do not apply to the work of Michaelis [8] on the dried collodion membrane where, owing to the very low permeability of the material to the solvent and solutes used, the concentration gradient remained practically constant during the whole of the experiment, and osmotic exchange was also negligible.

Our apparatus utilises the constant flow principle; it has been designed to eliminate as far as possible sources of uncertainty by maintaining a steady concentration gradient across the membrane, by careful adjustment of the opposing hydrostatic pressures and by rigid temperature control. The method has the further advantage that a check on the composition of the diffusate at short intervals is kept, so that alterations in the membrane itself may be followed. With electrolytes as solutes, this check is practically continuous, and enables impairment or failure of the membrane to be detected at once. In order to diminish the effects of unavoidable variation in the membrane itself, solutes are always studied in pairs, using one as a reference standard; this com-

[8] A. A. Weech and L. Michaelis, *J. Gen. Physiol.*, 1928, **12**, 55; also 1 above.

·parative method has other advantages in that variation of external conditions generally has then minimum influence on the results.

Experimental.

The apparatus is shown in Fig. 1; the central portion is the permeability cell A, which is given in detail in the inset. It consists of two flanged glass cups, 4 cm. in diameter, each provided with inlet and outlet as shown, and ground together to fit. The membrane B on a disc of hardened filter paper is held between these cups by two rubber rings which, after boiling in alkali and thorough washing, were proved not to contaminate the aqueous solutions in contact with their narrow inner edges. The two halves of the cell are held together by a thin rubber sleeve fitting tightly round the flanges, and by rubber rings held in wire clips (not shown in the figure). A solution of the solutes to be tested flows continuously through the upper compartment of the cell, and freshly distilled water flows through the lower compartment. The solution is contained in a 5-litre stock bottle C from which it runs to the constant level device D, the overflow being returned by a glass pump E to the stock bottle. From D the solution proceeds slowly through a narrow regulating capillary into the coils F, immersed in the thermostat G, and is delivered to the cell at constant temperature just above the membrane, from where it passes out by the tube H to the waste bottle J. The distilled water is obtained by continuous redistillation of the laboratory supply through a silica condenser K; from this, it passes directly to the constant level device L, the overflow finding its way to the receiver Q (immersed for

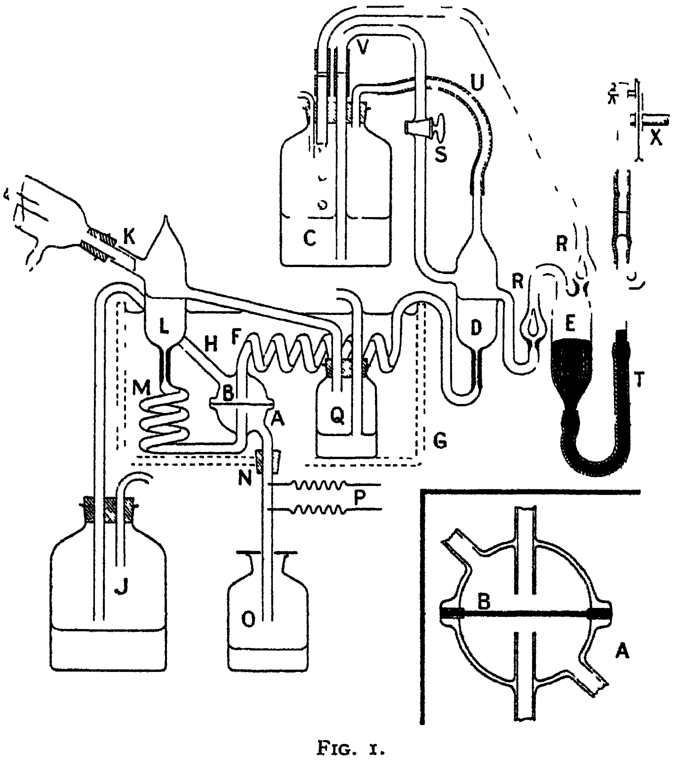

Fig. 1.

convenience in the thermostat) from which it is removed to waste by suction. Through a regulating capillary the water passes by the coils M to the lower compartment of the cell, where it is delivered at constant temperature just beneath the membrane; it then leaves by the tube N, which passes through the bottom of the thermostat, into the bottle O for analysis. Through the wall of the tube N two platinum wires P are fused about 1 cm. apart; these serve for controlling the electrical conductivity of the effluent. The pump E has a mercury piston which is given a rapid reciprocating motion of amplitude about 3 mm. by the eccentric wheel X; this wheel revolves about 300 times per minute, which speed is necessary to cause the flatly seated glass valves R to operate well. By regulation of the stopcock S, entry of air to the pump may be prevented; should air enter, however, change in concentration of the circulating liquid is rendered negligible by withdrawing this air from the stock bottle C through the rubber tube U. The pump rubber tubing T is boiled in alkali and thoroughly washed to avoid contamination of the mercury surface in E. The butted glass-rubber joints V are not essential, but very convenient in changing the solution in C; they are proved not to contaminate the solution. The whole apparatus and the containers are made from Jena 20 glass; except for the very small surfaces of exposed rubber, the solution comes into contact only with glass and the mercury in E, the distilled water and effluent only with silica, glass and the platinum wires P. The cell was proved to be free from leakage outwards by the introduction of concentrated dye solution, and from leakage inwards by placing salt solution in the thermostat, which made no appreciable increase in the electrical conductivity of the effluent when distilled water was passing through both compartments of the cell. The specific conductivity was measured with the usual bridge and galvanometer arrangement; that of the distilled water was 2×10^{-6} mhos. It was found sufficient to control the temperature of the thermostat to 0·1°.

To commence an experiment, the condenser is started and distilled water allowed to fill completely the lower half of the cell and tubes, the exit of N being shut temporarily by immersion in a tube containing mercury. The membrane is then slid into position, avoiding admission of air beneath it, and the upper half of the cell is adjusted and made secure. The incoming liquid then automatically displaces the air from the upper compartment, and as long as the capillary below L remains covered with distilled water, no air can enter the lower compartment. In the intervals between experiments, this is secured by closing the exit of N with mercury; the condenser may then be shut off. Should an air bubble inadvertently enter the lower compartment during the course of an experiment, it is likely to remain in the cell, and is not easily visible owing to the rubber sleeve round the cell. Its presence may, however, be detected at once when the diffusion of electrolytes is being studied by a sudden fall in the conductivity of the effluent as part of the membrane is rendered inactive. The air bubble is then easily removed into the tube N by momentary suction, and is quickly expelled. In our apparatus, the rate of flow of the solution through the cell is about 1 litre per hour, and of the distilled water about 400 c.c. per hour. These rates are controlled by the capillaries below the constant level tubes. The levels of solution and water in these tubes are the same, and so are the levels of the respective exits of the tubes H and N. Consequently the hydrostatic pressures on either side of the membrane are constant in any experiment and almost equal, that above the membrane being slightly less owing to the differential drag of the denser solution in comparison with that of the water. By this arrangement, solution and water pass through the cell at constant rates, and changes in the membrane such as alteration in permeability, or failure, may be detected by periodic analysis of the effluent. The membrane is well washed before placing in the cell; it is then washed in position by passing distilled water through both compartments until the conductivity of the effluent falls to 2×10^{-6} mhos. The water is then removed from D and the upper compartment of the cell as far as possible by suction through H, and the solution allowed to flow in, the effluent delivered by the pump being rejected for a few minutes. In a short time the effluent through H has the same composition as the stock solution in C. The effluent through N is collected and analysed at intervals; with electrolytes as solutes, the attainment of a steady state is indicated at once by the electrical conductivity. With an average cupric ferrocyanide membrane precipitated on hardened filter paper, about 0·15 millimol of NaCl per hour diffuses from a solution containing 100 millimols per litre, so that the hourly effluent of 400 c.c. is very dilute. As the lower side of the membrane clears itself rapidly of the solute diffusing through it, both by convection and by the delivery of fresh distilled water through M, a steady concentration gradient across the membrane between solution and distilled water is attained. Without interfering with this condition, the rate of flow of the distilled water may be considerably diminished; the increased concentration of the effluent makes analysis then simpler.

Discussion of the Method.

Effect of Membrane Support.

The best support for the membrane we have used is hardened filter paper; this by itself permits ready diffusion of solutes without measurable influence on their relative rates, and it is sufficiently firm and close-grained to hold a precipitated membrane satisfactorily. In testing the influence of a porous support on the relative diffusion rates of solutes, it is however necessary to balance carefully the opposing hydrostatic pressures in order to prevent gross bodily movement of the solution through the membrane, which would obscure any differential effect. Using this precaution with a solution equimolar with respect to NaCl and Na_2SO_4, we have never confirmed greater differences than 1 part in 1000 from the equimolar ratio of the salts in the diffusate.

Effect of Hydrostatic Pressure Difference.

With hardened filter paper alone in the cell, the total amount of solute transmitted from a given solution in unit time depends very greatly on the opposing hydrostatic pressures, as would be expected; this is also evident from gross changes in the volume of the effluent from the lower compartment of the cell with alteration of pressure. When the paper is properly impregnated with cupric ferrocyanide, however, the permeability to solvent and solutes is greatly diminished, and with it the sensitiveness to pressure differences; the volume of the lower effluent now shows only very small relative changes for pressure differences up to 20 mm. Hg. Owing to the low concentration of the effluent these changes correspond, however,

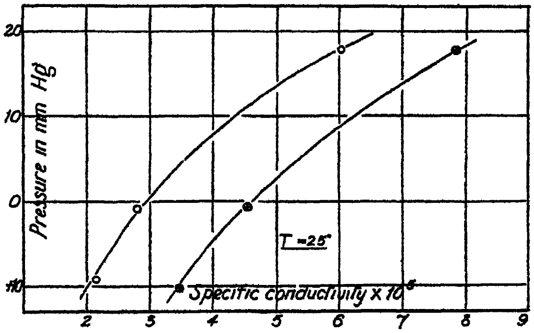

FIG. 2.

to considerable alteration in the amount of diffused solute. This is shown in Fig. 2, where pressure difference across the membrane is plotted against specific conductivity of effluent for two cupric ferrocyanide membranes, the upper solution in each case being 0·1 molar with respect to NaCl, and the distilled water passing below at 375 c.c. per hour. It will be observed that the conductivity of the effluent increases steadily with increase of pressure on the solution side of the membrane, and the necessity for careful control of the pressure is evident.

Effect of Concentration Gradient Across the Membrane.

The apparatus enables a detailed study of the relation between concentration gradient and concentration of the diffusate to be made; this is being done at present. The work is complicated by the great variation in properties shown by different membranes of the same material, but the results show generally that although the total solute diffused in unit time increases steadily with increasing concentration across the membrane as would be expected, yet the ratio in which two solutes diffuse together is almost independent of the concentration gradient, provided that this is the same for each solute during the test.

Effect of Variability of Membrane.

Our membranes were made by the method of Donnan and Allmand,[10] which proved to be the most satisfactory. In spite of all care, however, considerable differences between different membranes were found, not only in total amount of solutes transmitted in unit time, but also in the actual ratios of two solutes diffusing simultaneously from the same solution. A typical case is shown in Fig. 3, where a solution equimolar to NaCl and Na_2SO_4 (0·2 molar with respect to each) was tested with four different cupric ferrocyanide membranes. The curves show the molar ratio of chloride to sulphate transmitted against time in hours, the ratio in the original solution being preserved at unity. It will be seen that, after a preliminary period of usually less than one hour, the ratio transmitted by each membrane remains practically constant with

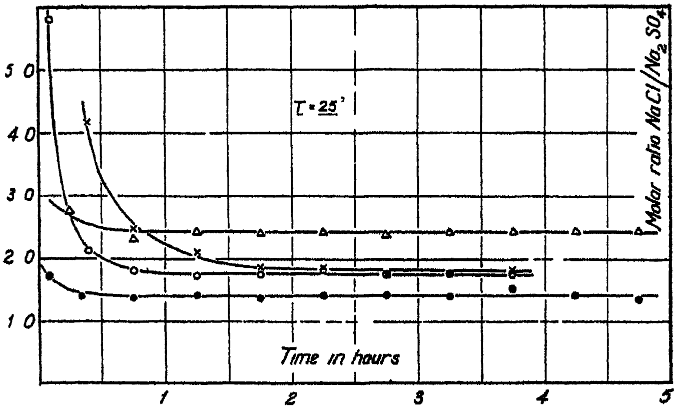

FIG. 3

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[10] F. G. Donnan and A. J. Allmand, *J. Chem. Soc.*, 1914, 105, 1941.

time, but the ratio varies from 1·4 to 2·4 in the different membranes. The ratio is usually much greater in the early period of a test, when the salt solution has not been long in contact with the washed membrane; during this period, the total amount of solute transmitted in unit time is less than in the later stages when it becomes approximately constant. It is probable, therefore, that this early variation is due to the gradual attainment of a steady concentration gradient across the membrane rather than to a change in the membrane itself. In most of the many tests performed, sucrose has been present in the solution in equal concentration with the salts, and its presence in the effluent has been sought by the Molisch reaction,[11] which may be made sensitive to 1 part in 10^7. In almost all cases, traces of sugar have appeared in the diffusate after some hours; in some cases the sugar appeared early and the accompanying low ratio of chloride to sulphate, combined with high transmission for the salts, made it evident that the membrane was definitely faulty. In one case where no sugar at all could be detected in the diffusate, the diffusion of the salts was also relatively slow and the chloride-sulphate ratio reached the high steady value of 4·5. These results show definitely that the method of making really good membranes which will function well in the absence of the membranogens requires further study; they point also to the value of the apparatus as a means of investigation.

Summary.

An apparatus for the accurate measurement of diffusion rates of solutes through membranes is described, and its advantages over previously used methods are discussed.

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[11] H. Molisch, *Monatshefte Chem*, 1886, 7, 198.

CATALYSIS IN HYDROCARBON CHEMISTRY (Parts IV. to VII.).

By R. H. Griffith.

Received 14*th December*, 1936.

PART IV.—THE ADSORPTION OF HEXANE ON CATALYSTS.

(With S. G. Hill.)

The fact that benzene, cyclohexane and hexane are adsorbed by molybdenum oxide catalysts at temperatures as high as 450° has already been demonstrated,[1] and the present investigation was carried out to compare the behaviour of a number of other metals or metallic oxides under similar conditions. A brief note of the results obtained has been given,[2] and this communication is concerned chiefly with recording the experimental data.

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[1] Griffith and Hill, *Proc. Roy. Soc. A*, 1935, 148, 194.

[2] Hollings and Griffith, *Nature*, 1932, 129, 834.

The catalysts were prepared in the form of an oxide, hydroxide or carbonate, either precipitated as such or purchased in the purest commercial grade available. The hydroxides of Al, Cr, Co, Cu, Fe, Mn and Ti were precipitated; Ca, Th, Zn, Zr, Mg, Pb and Sn were employed as oxides, vanadium was obtained by careful heating of pure ammonium vanadate, and tungsten was used as tungstic acid. In all cases the materials were carefully washed with distilled water until free from soluble matter. The dried solids were then finely powdered and made into a paste with water, extruded from a small handpress into threads, and broken into granules which were reduced in a stream of hydrogen at 450° for 50 hours.

The hexane was dried and redistilled before use, the same material being used throughout the whole series of experiments.

The adsorption apparatus was similar to that previously employed,[1] and gave the results recorded in Table I.; negative values appearing in this table indicate that decomposition of hexane has occurred, and the substances producing this effect are collected in group 1. The remaining substances did not lead to decomposition of hexane at 450°. In the expression of the volume of hydrocarbon adsorbed, the vapour is regarded as a true gas.

TABLE I.—C.c. (CORRECTED TO 0° AND 760 MM.) OF HEXANE ADSORBED BY 100 GRAMS OF CATALYST.

Group 1.	20°.	100°.	200°.	300°.	400°, 0 Hours.	400°, 2 Hours.	450°, 0 Hours.	450°, 2 Hours
Cr . .	250	208	126	66	98	7·8	—	—
Zn . .	8	—	1·6	2·3	1	−16·4	—	—
Fe . .	46	16	8·5	6	12	−63	—	—
Cu . .	23	17	16	−11 (after 1½ hours).			—	—
Charcoal .	—	—	140	85	47	−3·8	—	−38
Ti . .	—	—	57	27	29	—	22	−178
Mn . .	50	24	20	20	16·6	−19·5	—	—
W . .	28	25	10·5	8·7	6·0	−11	—	—
Co . .	—	—	14·6	15	12	−13	—	—
Al . .	130	45	19	17	19	—	17	−36
V . .	79	—	35	30	11	−108	—	—
Th . .	37	19	7·5	3	1	−6	—	—
Group 2.	**20°.**	**100°.**	**200°.**	**300°.**	**400°.**	**450°**		
Pb . .	11	5·4		5·2	5·4	4·1		
Mg . .	134	19	8		7·1	15		
Zr . .	92	30	18	16·2	16·4	16·6		
Ca . .	121	34	22	19	19	18·7		
Cd . .	82	47	51	54	60	63		
Sn . .	14	4		3·8	7	6·1		

It is clear that several types of adsorption of hexane can take place, varying in intensity, velocity and character. Although the existence of activated adsorption in the case of hydrocarbons is not nearly so obvious as it is with hydrogen, there is little doubt that it often takes place, but where decomposition occurs, the true effects are masked. There is also a qualitative relationship between activity for decomposition and one particular type of adsorption,[3] but it is evident that adsorption may lead to one of four results:

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[3] *Cf. The Mechanism of Contact Catalysis*, Oxford University Press, 1936, page 45.

(1) Vigorous decomposition causing extensive deposition of carbon on account of secondary reactions brought about by adsorption of primary reaction products;

(2) decomposition involving the loss of much hydrogen from the molecule;

(3) decomposition by loss of methane;

(4) holding of the molecule without decomposition.

Catalytic activity is therefore always accompanied by adsorption, but the existence of adsorption does not necessarily involve activity. These observations agree with the fact that decomposition of hydrocarbons is brought about by a very wide range of catalysts, and that the products obtained with the various contact materials employed are often very different one from the other.

Summary.

Comparative data are presented for the adsorption of hexane on a large number of catalysts at temperatures between 20° and 450°. Activated adsorption can be detected in many cases, and its relation to catalyst activity is discussed.

PART V.—PROMOTER CONCENTRATIONS.

In a previous communication,[4] the effect of the addition ot small amounts of silica was studied in relation to the activity of molybdenum oxide catalysts for the decomposition of hexane and cyclohexane.

A wide range of promoters has now been investigated by using the same method, in order to determine whether any regularity could be observed in the optimum concentration of the several substances. The results obtained have been described in outline,[5] and their significance has been discussed briefly.[6] The present communication is intended to provide experimental data supplementary to the previous notes.

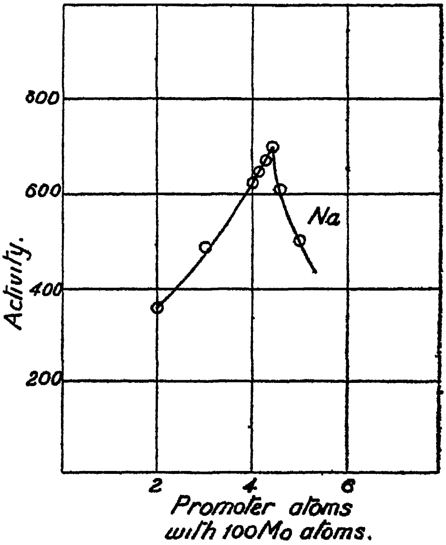

FIG. 1.

The substances employed as promoters were sodium, chromium, iron, copper, cerium, aluminium, barium, lead, boron and thorium. Sodium was added in the form of carbonate and reacted to give sodium molybdate; boron was added as boric acid. In the case of all the other substances, the molybdic acid was first treated with ammonia in order to give just sufficient ammonium molybdate to react with the promoter salt, which was either a nitrate or an acetate. This was found to be necessary in order to obtain uniform admixture of the promoter in such a form that it could not become unevenly distributed during subsequent drying and heating With mixtures containing sodium and boron, the catalyst threads were dried at room temperature, but the others could be dried in a steam oven

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[4] Griffith and Plant, *Proc. Roy. Soc. A*, 1935, 148, 191.

[5] Griffith, *Nature*, 1936, 137, 538.

[6] *The Mechanism of Contact Catalysis*, Oxford University Press, 1936, p. 77.

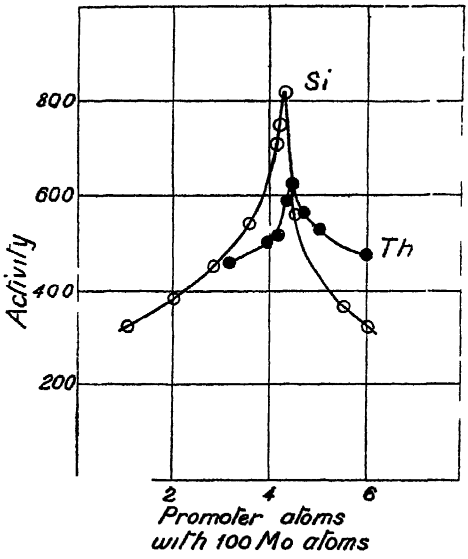

FIG. 2.

The granules employed were of the same size as before, the reaction temperature, method of experiment and expression of activity were also identical. Reduction was carried out at 500° for one hour with hydrogen at 100 c.c./minute before a test was begun.

Experimental results in addition to those previously published are shown in the accompanying drawings, which indicate the change in catalyst activity as the concentration of promoter was increased. The activity was determined by measuring the volume of permanent gas formed from hexane at 500° in unit time. In Table II. the positions and activity of the optimum are given. The latter are all corrected for the composition of the promoter compound as determined by analysis.

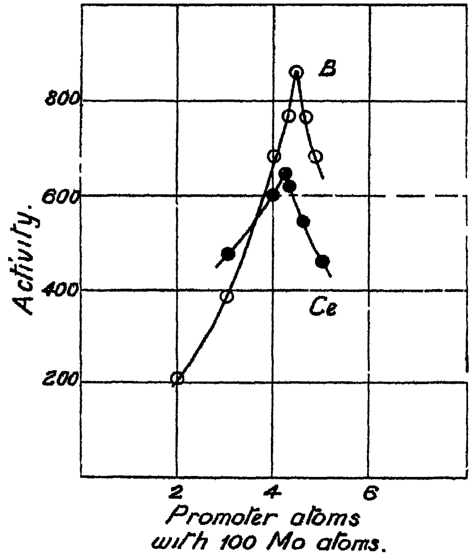

FIG. 3.

It is clear that the ten new promoters, and the silicon previously investigated, all fall into two classes. One of these has an optimum ratio of 4·3 to 4·4 atoms of promoter element to 100 atoms of molybdenum, and the other has a peak at half that concentration.

Also, it can be seen that those substances which are reduced to metals under the conditions of the experiments are all required in the smaller concentration, while those giving the peak at 4·4 atoms are all oxides. No difference in the optimum concentration can be observed with change in valency, density or crystal structure, and basic or acidic oxides behave similarly.

The actual value of the maximum activity, the rate of rise to this point, and of fall from it, does vary appreciably from case to case. It is probable, in view of the relatively high activity shown at points well beyond the maximum in the case of copper and thorium, that this final figure is determined by the activity of the promoter when employed alone as a catalyst. This means that the molybdenum surface has become completely covered with the promoter and is simply acting as a carrier for it.

TABLE II.—Position of Maximum Activity.

Promoter.	Concentration for Maximum.	Value of Maximum
Na . .	4·3	694
Cr . .	4·3	898
Ce . .	4·25	618
Al . .	4·6	950
Ba . .	4·3	833
B . .	4·3	844
Th . .	4·5	613
Si . .	4·3	825
Fe . .	2·1	1000
Cu . .	2·1	687
Pb . .	2·35	744

The volume of catalyst obtained from a given weight of molybdic acid, the initial activity measured at the beginning of a test, and the rate of fall to a final steady activity were found to vary considerably with the different promoters, but these factors do not affect the final results.

The promoter concentration required to give the optimum result with a given catalyst, for a particular reaction involving a single reactant, is therefore primarily a characteristic of the catalyst and not of the promoter. It follows that, once the position of the peak is known for any promoter for a given reaction with a single reactant, that of the others can be predicted.

A further deduction is that no higher activity can be obtained by the addition of a second promoter to the most active concentration of the first promoter, once the latter has been properly established. This point was confirmed by the addition of 0·1 atom of silicon, in the form of colloidal silica, to the chromium-promoted molybdenum catalyst of greatest activity. The result was a change of activity from 898 to 830.

Summary.

When a molybdenum oxide catalyst is promoted by the addition of another oxide, the concentration of the latter which gives the greatest activity is found to be the same in every case examined. The amount of promoter required is therefore a characteristic of the catalyst and not of the promoter oxide which is used. If the promoter is present as a metal, the concentration required is only half that which is necessary with an oxide. The prediction of the proper concentration of any promoter is therefore possible when that of any single one has been thoroughly established.

The significance of these results in connection with the general theory of catalysts is discussed.

PART VI.—THE CONVERSION OF PHENOL TO BENZENE.

The present investigation was carried out to determine the influence of changes in promoter concentration when two reactants were involved. The conversion of phenol to benzene, by treatment with hydrogen, appeared to be a particular interesting reaction of this type, as the products—water and benzene—were both of a different class from the two reactants, and were less likely to give rise to retardation similar to that previously observed in the hydrogenation of hydrocarbons.[7] The use of molybdenum oxide as a catalyst for this reaction is described by Fischer, Petrick and Bahr.[8]

Experimental Method.

An apparatus similar to that employed for the decomposition of hexane [9] was used with slight modifications. The saturator was constructed of copper, owing to the rapid attack of glass by hot phenol. The reaction tube was made of monel metal. A stream of dry hydrogen was passed at atmospheric pressure and at constant rate (207 c.c. per min.) into the phenol saturator at 100°, and thence to the catalyst tube at 440°. The catalysts were employed in the form of pellets and were prepared by the procedure previously described. The catalyst was reduced with hydrogen, not containing any phenol, for 30 minutes at 440° prior to each experiment.

The reaction products were cooled in a condenser and then passed to an electrostatic precipitator and through a tower packed with active charcoal, to a gas-collecting burette. As the vapour pressure of phenol at 100° is about 44 mm., the maximum contraction per minute would be about 13-14 c.c., depending somewhat on barometric pressure. No cyclohexane is produced from benzene under the conditions employed.[10] No liquid benzene would separate but its vapour was completely retained by the charcoal; strict precautions were taken that the latter did not become saturated and allow benzene vapour to pass to the gas collector. The course of the reaction was followed by measuring the volume of hydrogen collected per minute.

The volume of catalyst was chosen so that complete conversion to benzene was not quite achieved, and the results were then corrected to a standard catalyst volume of 10 c.c. measured after use. The activity is thus expressed as the contraction in volume of hydrogen per minute caused by 10 c.c. of catalyst. Although with molybdenum oxide alone the activity fell rapidly to zero in a few hours, generally it remained steady over periods of several hours in the case of catalysts containing appreciable concentrations of promoter (*e.g.* more than 2 atoms per 100), but for comparative purposes the experiments were continued for minutes in every case.

TABLE III.

Catalyst.	Absorption of H_2, c.c./minute.	Catalyst Volume, c.c.	Activity.
Ce 4 * .	6·6	5·0	13·2
8 .	7·5	6·0	12·5
12 .	6·0	4·6	13·1
16 .	6·0	4·0	15·0
66·6 .	7·0	4·8	14·6
Ce oxide	1·5	5	3·0
Na 4 .	0	4·5	0

* The compositions are given on the usual basis of promoter atoms to 100 molybdenum atoms; Ce 66·6 is cerium molybdate.

Results Obtained.

The two cases most fully investigated were molybdenum oxide promoted by silica and by alumina; the former was added as colloidal silica, and in the case of aluminium the nitrate was added to the molybdic acid containing just sufficient ammonia for its precipitation. A sharp peak in the concentration-activity curve[11] appeared at 15·0 atoms of Si to 100 atoms of Mo, and at 16·5 atoms of Al. Experiments were also carried out with boric acid, but although a promoting effect was observed, it was erratic and not reproducible. The catalysts containing boric acid were also found to be covered with a fine crystalline deposit after use, and it was evident that volatilisation of boric acid, by means of the steam formed in the reaction, was leading to these irregularities.

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[7] *Proc. Roy. Soc. A*, 1935, **148**, 186.

[8] *Brennstoff-Chemie*, 1932, **13**, 45.

[9] *Proc. Roy. Soc. A*, 1935, **148**, 191.

[10] Sabatier and Mailhe, *Compt. Rend.*, 1903, **137**, 240; Burrows and Lucarini, *J. Amer. Chem. Soc.*, 1927, **49**, 1157.

[11] *Cf. The Mechanism of Contact Catalysis*, Oxford University Press, 1936, p. 79.

Other experiments, with sodium added as carbonate and with cerium, precipitated as molybdate, are recorded in Table III.; the former gave no promoting effect and the latter gave an activity figure which remained practically unaltered between atomic ratios of 4 and 66·6 to 100.

Discussion.

From these results it is possible to draw the following conclusions: (1) the concentration of promoter required to give the maximum effect is different from that observed in the case of hydrocarbon decomposition; (2) the optimum concentration does not remain unaltered by the use of different promoters, although the results are still close together.

(1) This fact indicates that different classes of reactants are absorbed by different parts of the catalyst surface.

(2) Two alternative explanations of this effect may be suggested: (*a*) that the small differences previously observed in the case of hexane decomposition are real differences. It is interesting to observe that the ratio of Al to Si in the former case is 1·07 and in the present case is 1·10; (*b*) that the observed promoting effect, when two reactants are involved, is primarily due to the increase in the rate of adsorption of that reactant which is normally more slowly adsorbed. When the maximum promoting effect, with regard to the latter, is approached, its adsorption velocity may become of the same order as, or even greater than, that of the second reactant, so that the influence of promoter concentration on the latter also plays its part. This would lead to displacement of the observed optimum unless every promoter gives the same degree of effect as well as the same position.

It has already been shown (Part V.) that the degree of effect obtained varies with the promoter employed, and it seems that the second alternative is the more likely explanation of the results now recorded.

The behaviour of sodium and cerium may at first appear to disagree with earlier statements that any oxide can act as a promoter, provided that it is added in uniform distribution. In fact, however, they can be readily explained as cases of compound formation in which the compounds have a specific effect and excess molybdenum oxide simply acts as a carrier; the substance obtained by reduction of sodium molybdate is inactive, while that from cerium molybdate gives a fairly high activity. This is confirmed by the fact that cerium oxide alone is also found to have a very small activity.

It is interesting to observe that aluminium is stated not to form a molybdate.[12]

It is therefore evident that although both sodium and cerium molybdates appeared to be completely decomposed at 500° in contact with hexane, since they gave true promoter curves, yet they retain their intimate association in the form of a compound at 440° in contact with phenol and hydrogen. Unfortunately comparative experiments at 500° in the present case are not possible as the catalysts lose their activity

[12] *J. prakt. Chem.*, 1854, 61, 453; 1860, 81, 411.

so rapidly at that temperature, owing to the deposition of decomposition products. This fact greatly limits the number of possible true promoters in the present case.

The results described in this paper should be compared with those obtained by Kingman and Rideal[13] when using heteropoly acids containing molybdenum, as catalysts for phenol reduction. These authors showed that the compound acids fell into two classes, those containing P, Ni, Cr and Si giving increased activity, while those with Sn and Th in the molecule were less effective than molybdenum oxide alone. The catalysts obtained in this way cannot, however, be considered as promoted in the sense used above, and they must be classified as compound catalysts instead, each compound having its own characteristic activity.

Summary.

The effect of promoters on molybdenum oxide as a catalyst for the deoxidation of phenol by means of hydrogen at atmospheric pressure is discussed.

It is found that the optimum concentration of promoter is different from that required in the case of hexane decomposition, and is also slightly dependent on the particular promoter employed.

Compound formation is found to occur in certain cases, and give effects which can be easily distinguished from those of true promoter action.

PART VII.—CARRIER ACTION AND MOLECULE SIZE.

In a previous communication,[14] attention was called to the fact that with molybdenum catalysts, used for the hydrogenation of tar oils under pressure, no change in activity was observed when an appreciable quantity of an inert material was added to the pure catalyst. A similar observation is recorded in an annual report of the Fuel Research Board (1934, p. 80).

The most likely explanation of this phenomenon appeared to be that the reacting hydrocarbon molecule was so large relatively to the distance between the active centres of the catalysts that only a small proportion of the latter were actually effective in the case of the pure catalyst, and that addition of the inert material showed no diluting effect because there was still a sufficient number of active centres.

A closer study of this point has now been made by following the dehydrogenation of dekalin, decane, hexane and cyclohexane in contact with various catalysts at ordinary pressures. The experimental method was that previously employed with hexane, slightly modified to suit a wider range of conditions.

A stream of nitrogen (83 c.c. per minute dry at 0° and 760 mm.) was passed over the hydrocarbon in a saturator maintained at such a temperature that the vapour pressure of the latter was 160 mm. in each case, and the mixture then came in contact with the catalyst at 500°. The catalyst was previously reduced with pure hydrogen. The activity of the catalyst was expressed as the volume of permanent gas, dry at 0° and 760 mm., produced by 100 c.c. of catalyst per minute. In every case experiments were continued until a steady activity of the catalyst was shown for at east two ho urs.

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[13] *Nature*, 1936, **137**, 529. [14] *Proc. Roy. Soc. A*, 1935, **148**, 186.

Hydrocarbons Used.

Dekalin was redistilled before use, and the product actually employed was found to contain both cis- and trans-dekalin, as well as a small quantity of tetralin. Separate experiments carried out with very carefully prepared samples of the two stereoisomers showed that cis- form was decomposed slightly more easily than the trans-, as would be expected. It was also found that tetralin was more reactive than either form of the fully saturated molecule, but the rigorous purification of the hydrocarbons was not necessary for the series of experiments on carrier action.

Decane was prepared from a commercial " white spirit " by washing with strong sulphuric acid, extracting the residue with warm aniline and fractionating the product to a boiling-point of 171-173°. It was not pure hydrocarbon but representative of a long-chain type. Hexane and cyclohexane were redistilled commercial products.

Preparation of Catalysts.

Titanium hydroxide was prepared by precipitation from a solution of titanic chloride, followed by washing of the precipitate until free from chloride. The air-dried product was ground in a paint mill before use. (This method was applied in every subsequent case as well.) Copper oxide, of analytical reagent quality, was used for preparation of copper catalysts, and chromium hydroxide was obtained by precipitation from chrome-alum, also of analytical reagent quality.

As carrier, pure magnesium oxide was chiefly employed. It was selected on account of its inert character towards hydrocarbons (*cf.* Part IV.), but a few parallel experiments were carried out with molybdic acid, and with china clay as carriers. The carriers were all incorporated by mechanical mixing with the catalyst. In every case the catalyst was used in the form of small pellets, as described in previous publications.

Experimental Data.

In Table IV. are given results obtained with titanium and copper catalysts used with dekalin. It is evident that, with the former, a

TABLE IV.—DECOMPOSITION OF DEKALIN.

Catalyst.	C.c. Gas, per Min.	C.c. Catalyst.	Activity.
100 per cent Titanium oxide . . .	23·0	8·0	287
80 ,, ,, ,, 20 per cent. MgO	19·0	8·1	234
70 ,, ,, ,, 30 ,, ,,	16·5	8·1	203
60 ,, ,, ,, 40 ,, ,,	14·5	8·2	177
50 ,, ,, ,, 50 ,, ,,	11·0	7·9	139
20 ,, ,, ,, 80 ,, ,,	6·0	8·2	73
10 ,, ,, ,, 90 ,, ,,	4·0	8·8	45
0 ,, ,, ,, 100 ,, ,,	0·5	10·0	5
100 per cent Copper oxide . . .	0		0
90 ,, ,, ,, 10 per cent. MgO	9·0	10·5	85·7
80 ,, ,, ,, 20 ,, ,,	9·75	11·2	85·7
70 ,, ,, ,, 30 ,, ,,	10·8	12·8	84·4
50 ,, ,, ,, 50 ,, ,,	12·2	14·2	85·5
30 ,, ,, ,, 70 ,, ,,	16·2	18·3	88·5
10 ,, ,, ,, 90 ,, ,,	8·5	13·2	64·4
5 ,, ,, ,, 95 ,, ,,	4·6	13·6	33·8
60 per cent. Titanium oxide . .	9·5	6·4	150
40 ,, Molybdic acid . .			
30 ,, Chromium oxide . .	5·7	5·9	97
70 ,, Molybdic acid . .			

straight dilution effect sets in on the addition of carrier, and it may be concluded that this catalyst only contains a small number of active centres. With copper, however, the results are different. The pure oxide is found to give a catalyst whose activity rapidly falls to zero and this is due to sintering of the metallic copper. With the addition of 10 per cent. of magnesia, however, this change is prevented. On the further addition of magnesia a steady activity persists until the mixture contains only 10 per cent. of copper oxide; the 5 per cent. mixture is again lower.

The case of copper, therefore, appeared to be suitable for further study except for the fact that the 10 per cent. and 5 per cent. mixtures were not reduced to metallic copper during the experiment. This is undoubtedly a disturbing factor, and renders the substance useless for the present investigation.

Chromium Catalysts.

The results obtained with chromium oxide are given in Table V. It is here clearly indicated that the concentration of inert carrier which may be added, before dilution sets in, depends on the size of the reacting molecule. As would be expected, the greater dilution is possible the larger the molecule, the whole catalyst surface being accessible to hexane but only a small proportion to dekalin. The case of cyclohexane (Table VI.) is anomalous, as the catalyst was not reduced to the same oxide. The black oxide was formed in every case but that of cyclohexane, the colour appearing equally intense even with high concentration of carrier, but the change in intensity with the green-brown oxide was pronounced. If previously reduced black oxide was used with

TABLE V.—DECOMPOSITION OF HYDROCARBONS WITH CHROMIUM OXIDE CATALYSTS CONTAINING MAGNESIA AS CARRIER.

Hydrocarbon.	Catalyst per cent., Cr Oxide	C.c. Gas, per Min.	C.c. Catalyst.	Activity.
Dekalin .	100	9·0	9·0	100
,, .	50	17·0	17·0	100
,, .	30	17·1	17·6	97
,, .	10	16·1	16·2	99
,, .	5	13·8	18·0	77
,, .	0	0·5	10·0	5
Decane .	100	5·1	9·0	56·7
,, . .	50	9·1	16·5	55·1
,, . .	20	5·7	16·8	34·0
,, . .	10	3·1	17·5	17·7
,, . .	0	0	—	0
Hexane .	100	2·15	8·6	25
,, . .	80	2·95	13·4	22
,, . .	50	2·0	10·2	12·4
,, . .	10	0 35	17·5	2·0
,, . .	0	0	—	0
Cyclohexane .	100	18·0	9·0	200
,, .	50	7·7	16·8	46
,, .	10	0·35	17·6	2
,, .	0	0	—	0
,, .	100 after dekalin	0·35	9·6	4

cyclohexane the activity was so low that the dilution effect could not be followed.

TABLE VI.—Decomposition of Dekalin with Cr Oxide-silica Catalyst.

Carrier.	C.c. Gas per Min.	C.c. Catalyst.	Activity.
0 per cent.	13·0	4·8	271
10 per cent. MgO	11·95	5·3	225·5
20 ,, ,,	9·8	6·1	160·7
30 ,, ,,	8·0	7·4	108
50 ,, ,,	8·6	8·1	106
70 ,, ,,	7·7	8·8	87·5
80 ,, ,,	7·0	8·9	76·7
90 ,, ,,	5·6	9·3	60·2
95 ,, ,,	2·75	9·0	30·6
20 ,, Molybdic acid	6·9	3·0	230
40 ,, ,, ,,	6·3	4·0	160
60 ,, ,, ,,	4·0	4·8	83·3
70 ,, ,, ,,	6·15	8·8	70
80 ,, ,, ,,	2·15	3·6	58·3
25 ,, China clay	7·65	6·3	121·5
50 ,, ,,	5·5	6·4	85·9
80 ,, ,,	4·2	9·8	42·4

Promoted Chromium.

These observations suggested that parallel experiments with a promoted chromium catalyst would indicate whether the latter contained a larger number of active centres than the unpromoted catalyst. Mixtures of chromium oxide and colloidal silica were therefore prepared in order to discover the optimum promoter concentration. The promoted catalyst was mixed, as before, with carrier.

The results given in Table VI. show that an entirely different state of affairs exists on the surface of the promoted catalyst. Regardless of the nature of the carrier an immediate dilution sets in in every case. It must, therefore, be concluded that the promoter does not increase the number of active centres but produces others of an entirely distinct type. This deduction agrees with those arrived at by other methods.[15]

Summary.

(1) The most active catalyst does not necessarily have the largest number of active centres.

(2) The lowering effects observed with carriers cannot be due to compound formation with the catalyst as similar results are given by substances of widely different character.

(3) With a catalyst containing a large number of active centres the addition of a carrier will produce a lowering of activity at a concentration which depends on the size of the reacting molecule.

(4) The addition of a promoter does not increase the number of active centres but produces a surface of a different type from that of the pure catalyst.

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[15] *Cf. The Mechanism of Contact Catalysis*, Oxford University Press, 1936, p. 177.

(5) Changes in activity occur if the degree of reduction of an oxide catalyst varies; this type of change is associated with visible colour differences.

(6) A carrier may produce an initial increase in the activity of a catalyst by prevention of sintering.

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TWO RULES CONCERNING SOLUBILITY OF GASES AND CRUDE DATA ON SOLUBILITY OF KRYPTON.

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Many attempts have been made to discover regularities in the solubility of gases; G. Just[1] found that the order of solution capacity of any solvent is about the same for all gases and that the solubility of one gas in a solvent can be found approximately by multiplying its solubility in another solvent by a factor which depends only on the solvents and not on the gases. There is, however, a series of exceptions from this rule. Just[1] observed also a negative correlation between the refractive index and the dissolving power of solvents; F. W. Skirrow[2] and A. Christoff[3] found that surface tension and dissolving capacity are negatively correlated. J. H. Hildebrand[4] discussed the influence of cohesive forces on solubility and expressed a series of cohesional phenomena in terms of internal pressure. The most interesting relation, namely that between electric polarisability, dipole moment and solvent power, was examined by B. Sisskind and J. S. Kasarnovsky.[5] An increase in any of the two former factors causes the solvent power to increase.

So long as the gas is below its critical temperature the laws governing its solubility are special cases of the relations between the vapour pressure and composition above binary liquid systems. This aspect of the problem is treated extensively by van der Waals,[6] by Horiuti[7] and by Hildebrand.[8] In the simplest case, when Raoult's law is valid for the binary mixture, the molar solubility of any gas is independent of the nature of the solvent and inversely proportional to the saturation pressure

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[*] This work was carried out with the assistance of L. Weisz, to whom I am greatly indebted.

[1] G. Just, *Z. physik. Chem.*, 1901, **37**, 342.

[2] F. W. Skirrow *ibid.*, 1902, **41**, 139.

[3] A. Christoff, *ibid.*, 1905, **53**, 321.

[4] J. H. Hildebrand, *Solubility*, 1936, pp. 133-140.

[5] B. Sisskind and J. S. Kasarnovsky, *Zeitschr. anorg. allg. Chem.*, 1933, **214**, 385.

[6] J. D. van der Waals, *Lehrbuch der Thermodynamik*, 1912, pp. 169 and 617.

[7] J. Horiuti, *Scient. Papers Inst. Physik. Chem. Research*, Tokyo, 1931, **17**, 125.

[8] J. H. Hildebrand, *loc. cit.*,[4] pp. 26-31.

of the solute gas at the given temperature. It is interesting that if the saturation pressure may be extrapolated logarithmically above the critical point, the above relation still remains valid with this fictitious saturation pressure, although the system can, of course, no longer be considered as a mixture of two liquids. Van der Waals and Horiuti extend their calculations to the case where the validity of Raoult's law is not postulated. Van der Waals arrives at a semi-empirical equation, where solubility is expressed as a function of the critical temperatures and pressures of the components and the derivates of the critical constants *of the mixture* by the composition. Horiuti in his experimental paper derives two semi-empirical equations with four and five empirical constants respectively, on a similar basis, and calculates the molar solubilities of a series of gases in a series of solvents in good agreement with his measurements.

Solubility of Gases as a Function of their Critical Temperature.

Assuming that the Boltzmann equation holds for the relative concentrations of a gas in the solvent and in the gas phase, we plotted directly the logarithm of molar solubility as a function of the different "cohesive" properties of the solute gases. The basic assumption was, that a gas in which there are strong cohesive forces acting between its own molecules will be acted upon strongly by the solvent. We found that the logarithm of solubility is nearly a linear function of the critical temperature of the gas and that the slope of these straight lines is about the same for all solvents, as seen in Figs. 1-3, where solubility data at 20° C.

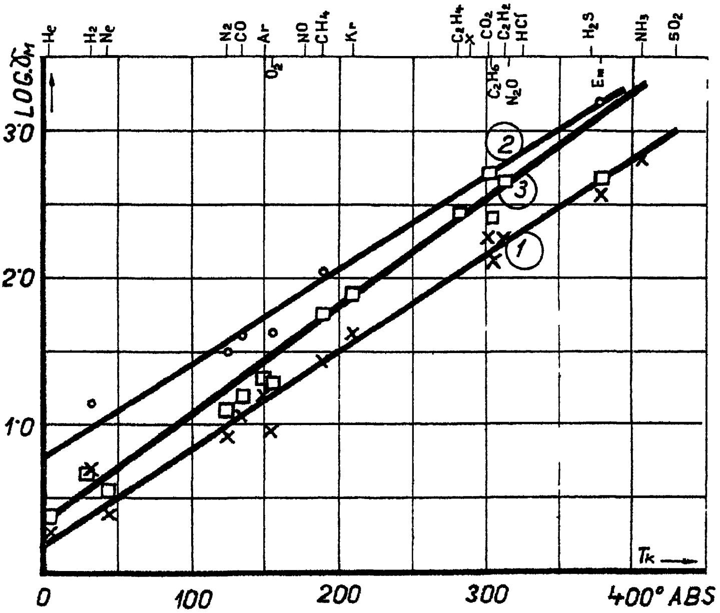

FIG. 1.—Curve 1, ethyl alcohol; curve 2, ethyl ether; curve 3, acetone. (*Note.*—A point on curve 3 at T_k 320, log γ_M 3·25 has been omitted.)

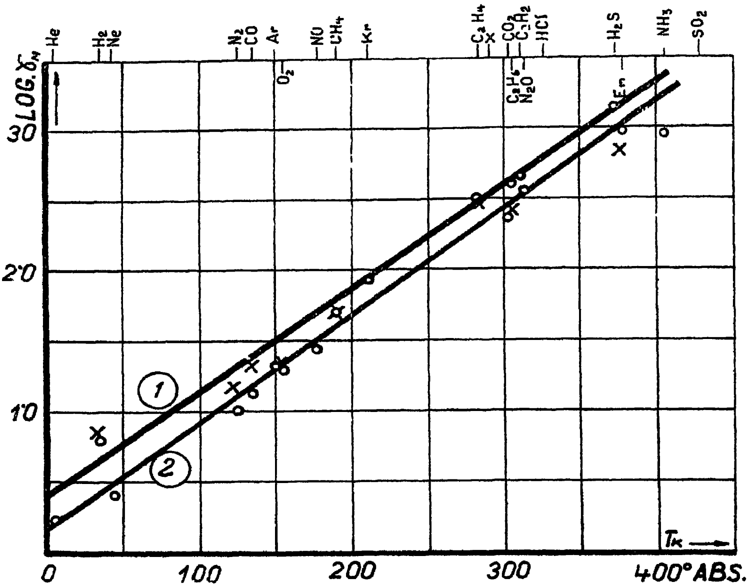

FIG. 2.—Curve 1, methyl acetate; curve 2, benzene.
(*Note.*—A point on curve 1 at T_k 320 and log γ_M 3·25 has been omitted.)

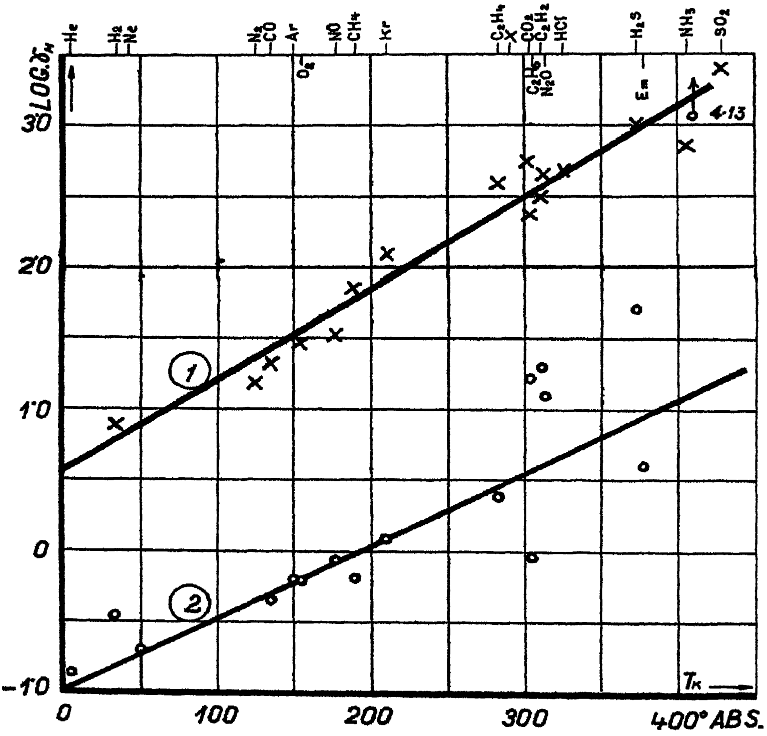

FIG. 3.—Curve 1, tetrachloromethane; curve 2, water.

20° C. are plotted. We calculated the positionof the straight lines by the method of least squares, except in the case of the graph of water where the gases which dissolve to form ions are disregarded. Nine other solvents gave quite similar results, but their graphs are not published, in order to save space. In Table I., however, the slopes (tg_α) and the intercepts (a) of all these fifteen straight lines are given, together with the standard deviation of the data from these straight lines. The experimental data are from the tables of Landolt-Börnstein and contain all those solvents of which the gas-dissolving capacity has been sufficiently investigated.

TABLE I.

Solvent.	tg_α.	a.	Standard Deviation of log. Solubility.
Methyl alcohol	0·0062	0·11	0·11
Ethyl alcohol. (Fig. 1) . . .	0·0064	0·22	0·12
Amyl alcohol	0·0068	0·31	0·07
Ethyl ether. (Fig. 1) . . .	0·0062	0·79	0·10
Acetone. (Fig. 1)	0·0072	0·34	0·23
Methyl acetate. (Fig. 2) . .	0·0071	0·41	0·28
Ethylacetate	0·0066	0·42	0·16
Benzene. (Fig. 2)	0·0079	0·18	0·19
Toluene	0·0059	0·67	0·27
Xylene	0·0056	0·63	0·15
Cyclohexane	0·0071	0·42	0·13
Cyclohexanol	0·0057	0·29	0·40
Tetrachloromethane. (Fig. 3) .	0·0063	0·58	0·16
Chloroform	0·0083	0·15	0·16
Chlorobenzene	0·0084	0·05	0·18

It is surprising that this relation should hold for a range of solubility from about 1 to 1000 for gases so different as, for instance, helium and sulphur dioxide. One necessarily infers that gas solubility is governed to a first approximation by " physical " forces, while " chemical affinity " only modifies their action to a small extent and probably causes the deviation of certain points from the straight lines.

There are two systematic exceptions from our rule, *viz.* water as solvent and hydrogen as solute. It is not surprising that water with its extreme properties, strong association, large dielectric constant and small thermal expansion, should give somewhat inconsistent results. The strongly ionised solutes (HCl, SO_2, NH_3) dissolve to a far greater extent than any other gas ; they are not strictly comparable with the others. H_2S, CO_2 and C_2H_2 ionise to a smaller extent and accordingly their solubility lies not so far above the straight line. Acetylene forms compounds with water and some organic solvents and this may account for its abnormally large solubility. It would be interesting to see whether some very bad fits, *e.g.*, CO in cyclohexanol, NH_3 in CCl_4 and Em in acetone would be confirmed by new measurements. The new, extremely precise, data of Horiuti [7] fit better into the logarithmic graphs than the old ones. Hydrogen, however, systematically dissolves much better in all solvents than could be expected from the logarithmic relation. We found no explanation for this phenomenon ; possibly, solubility determinations on deuterium would help to understand it better.

Evidence of a qualitative correlation between solubility and critical temperature is stated by Hildebrand.[9] A quantitative semi-empirical relation, similar to that of van der Waals, may be derived as follows: The Ostwald solubility for a mol solvent is defined as

$$\gamma_M = \frac{\text{gas dissolved in 1 mol solvent}}{\text{gas concentr. in gas phase}} = \frac{C \,.\, V}{c} \quad . \quad . \quad (1)$$

where C and c are the molar concentrations of the gas in the solvent and in the gas phase respectively and V is the molar volume of the solvent. If the gas law $p = c \,.\, R \,.\, T$ holds in the gas phase, if the vapour pressure of the solvent may be neglected and Raoult's law is valid ($p = C \,.\, P$), we have

$$\gamma_M = \frac{R \,.\, T \;\; V}{P} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where P stands for the saturation pressure of the gas. We now introduce the semi-empirical vapour pressure equation of van der Waals:[10]

$$\log \frac{P_k}{P} = f \,.\left(\frac{T_k}{T} - 1\right) \quad . \quad . \quad . \quad . \quad (3)$$

where P_k and T_k are critical constants of the gas and f is a numerical constant with an empirical value between 2·5 and 3. Combining (3) with (2) we obtain:

$$\log \gamma_M = \text{const.} - \log P_k + f\frac{T_k}{T} \quad . \quad . \quad . \quad (4)$$

Thus if P_k were the same for all gases, relation (4) would account for the linearity of log γ_M against T_k with a slope of the straight lines (f/T) between 0·0083 and 0·0100, whereas the effective slopes range from 0·0056 to 0·0083 (see Table I.). As mentioned above, the solubility of H_2 does not fit into either of the straight lines: it lies systematically higher. We wondered, therefore, whether the exact equation (4) would give a better agreement and plotted log γ_M against $-\log P_k + \frac{f \,.\, T_k}{T}$: the result gave a still greater deviation of H_2 from the straight lines. Thus it seems that our empirical relation:

$$\log \gamma_M = A + B \,.\, T_k \quad . \quad . \quad . \quad . \quad (5)$$

is at least as good an approximation to the facts as formula (4). Moreover, the T_k of the gases from helium to ethylene lies below room temperature, so that theoretical derivations based upon the theory of binary mixtures necessarily use the extrapolation of a non-existing vapour pressure above the critical temperature. Formula (5), on the other hand, may serve as simple empirical relation between solubility and T_k.

It can be shown that Just's law (see above) would be a consequence of (5) if B were the same for all solvents. Writing the solubility of a gas in one solvent as γ and in the other solvent as γ' and the constants of (5) as A, B and A', B', respectively, we can express equation (5) for each solvent, subtract the two equations, and write the difference in the exponential form:

$$\frac{\gamma}{\gamma'} = e^{A-A'} \,.\, e^{(B-B') \,.\, T_k} \quad . \quad . \quad . \quad . \quad (6)$$

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[9] *Loc. cit.*,[4] p. 32. [10] Geiger-Scheel, *Handbuch der Physik*, vol. x., p. 168.

It is only in the special case when B and B' are equal that the second exponential expression disappears, to yield:

$$\frac{\gamma}{\gamma'} = e^{A-A'} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

A and A' are characteristics of the *solvents* and the right side of equation (7) is thus *independent of the gases.* In other words, the solubilities of any gas in two solvents stand in a constant ratio which is independent of the gas and depends only on the two solvents in question (Just's law). Since B and B' are often not strictly equal, Just's law cannot be strictly valid; this accords with the experimental facts. We are indebted to Dr. P. Csillag for the derivation of Just's law from the constancy of B.

The Temperature Coefficient of Gas Solubility.

It is frequently assumed that all gases dissolve to a greater extent at low than at high temperatures. A glance at the Landolt-Börnstein tables, however, shows that this is not so: there are a large number of gases which dissolve better when the temperature increases. We found that the sign of the temperature coefficient of solubility is a function of the cohesive forces acting between the gas molecules. The solute gases are arranged in Table II., again in order of their critical temperatures; the data in the table are the temperature derivates of molar solubilities $\frac{\Delta\gamma_M}{\Delta T}$ at about 20° C., where γ_M is the number of c.c. of gas dissolved in one mol of solvent. The result of this juxtaposition is striking: all gases with low critical temperature (low cohesional forces) and small solubility have a positive temperature coefficient of solubility. Evidently the rule of Hildebrand, that solubility varies inversely with the vapour pressure of the solute, ceases to hold at so great a distance above the critical temperature. The gases with a T_k above 180° K. behave in the manner generally expected of gases: their solubility decreases with increasing temperature. There are hardly any exceptions from this rule, the most serious one being water as solvent in which all gases, even helium, have a negative temperature coefficient of solubility.

It is conceivable that the cohesive force between the solvent molecules is higher than the attraction between them and the intruding gas, so that the gas has to pay with its thermal energy for its intrusion into the liquid and thus dissolves the better the higher the temperature. Solubility may thus be expressed by a Boltzmann equation

$$\gamma = A(T) \, . \, e^{\frac{V-U}{kT}} \quad . \quad . \quad . \quad . \quad (8)$$

where U denotes the cohesion between solvent molecules, V the cohesion between solvent and gas molecules and $A(T)$ the steric factor of the process. Neglecting the temperature dependence of $A(T)$, γ increases with the temperature only when $U > V$.

Professor Polanyi has suggested to the author that $\frac{dA(T)}{dT}$ cannot be neglected and that it is just this quantity which gives to the least soluble gases a positive temperature coefficient of solubility. According to this view $\left(\frac{\partial\gamma}{\partial T}\right)_V$ should be always negative. The experimentally

TABLE II.—TEMPERATURE COEFFICIENT OF SOLUBILITY *

Gas	He	H_2	Ne	N_2	CO	Ar	O_2	NO	CH_4	C_2H_4	X	CO_2	C_2H_6	C_2H_2	N_2O	Em	NH_3	SO_2
T_k abs.°	5·2	33	44	126	134	151	155	177	191	283	290	304	305	309	310	378	405	428
Solvent:																		
Water	0·0	— 0·0022	— 0·0007	— 0·004	— 0·007	— 0·01	— 0·01	0·01	— 0·01	— 0·05	— 0·05	— 0·46	— 2·16	— 0·33	— 0·29	— 0·10	— 306	— 27
Methyl alcohol	+ 0·02	+ 0·03	+ 0·02	+ 0·06	+ 0·10	0·0	— 0·13		— 0·08	— 2·2		— 1·6	— 0·75		— 0·88	— 5·6		
Ethyl alcohol	+ 0·02	+ 0·03	+ 0·03	+ 0·04	+ 0·02	+ 0·01			— 0·09			— 1 98	— 0·80		— 2·1	— 6·8	— 205	
Amyl alcohol		+ 0·04		+ 0·04	0·0				— 0·12			— 2·4			— 2·7	— 13		
Ccylohexanol	+ 0·02		+ 0·03			+ 0·06												
Ethylether		+ 0·11		+ 0·10	+ 0·06		+ 0·09		— 0·42			— 12				— 34	— 44	
Acetone	+ 0·04	+ 0·07	+ 0·05	+ 0·07	+ 0·13	+ 0·10	+ 0·07		— 0·60	— 3·0		— 8·8	— 2·4	— 47	— 8·3	— 6·9		— 147
Acetic acid		+ 0·02		+ 0·02	+ 0·02							— 4·7			— 4·4	— 3·2		
Methyl acetate		+ 0·06		+ 0·08	+ 0·07		+ 0·08		— 0·02	— 3·0			— 2·7	— 41	— 9·4			— 386
Ethyl acetate		+ 0·12		+ 0·10	+ 0·19								— 0·24			— 10 5		
Butyl acetate		+ 0·10		+ 0·07	+ 0·10							— 6·15						
Amyl acetate		+ 0·09		+ 0·09	+ 0·09							— 7·45	— 3·55		— 7 6	— 31		
Chloroform				+ 0·11	+ 0·08							— 4·4			— 7·1	— 24		
Carbon tetrachloride		+ 0·07		+ 0·08	+ 0·08		+ 0·07	+ 0·06	— 0·18	— 4·1		— 4·1	— 6·8	— 3·3	— 5·6			— 81
Chlorobenzene		+ 0·05		+ 0·06	+ 0·06		+ 0·06		— 0·04	— 2·7		— 3·3	— 4·5	— 5·35	— 4·3			— 185
Nitrobenzene		+ 0·04		+ 0·04	+ 0·05				+ 0·01			— 4·1					— 39	
Aniline		— 0·04		+ 0·00	+ 0 05						— 3·4	— 1·5			— 1·2	— 3 2		
Carbon disulphide		+ 0·05		+ 0·07	+ 0·02							— 0·23				— 37		
Benzene	+ 0·04	+ 0·06	+ 0·04	+ 0·07	+ 0·12	+ 0 09	+ 0·09	+ 0·05	— 0·01	— 3·4		— 2·1	— 4·3	— 6·9	— 45	— 30		— 263
Toluene		+ 0·08		+ 0·10	+ 0 15				— 0·37			— 2·8				— 31	— 104	
Xylene		+ 0·09		+ 0·10	+ 0·10				— 0·16			— 3·2				— 28		
Cylohexane	+ 0·05		+ 0·07			+ 0·09												
Hexane									— 0·54	— 2·1			— 2·9			— 51		

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* The data on the temperature dependence of solubility are even more divergent than the solubility data themselves by different authors

observed derivate $\left(\frac{\partial\gamma}{\partial T}\right)_\pi$ would only be positive as a consequence of the thermal expansion of the liquid: the free space available for solution increases with the temperature. The hydrostatic pressure π affects only the liquid phase (*e.g.*, by means of a semi-permeable membrane) and it must be raised to compensate the thermal expansion of the liquid. The negative $\left(\frac{\partial\gamma}{\partial T}\right)_\pi$ of *all gases in water* at room temperature is easy to explain on this basis: the thermal expansion of water is nearly zero at this temperature.

We calculate $\left(\frac{\partial\gamma}{\partial T}\right)_V$ from $\left(\frac{\delta\gamma}{\delta T}\right)_\pi$, using the laws of thermodynamics. In equilibrium, the thermodynamic potential of the liquid and gas phase must remain constant for a variation in the concentration of the solute gas. Remembering that the pressure in the gas phase (p) and in the liquid (π) are not equal and summing up the terms of the specific thermodynamic potentials which are independent of p, π and c in $\psi_{1\,\text{gas}}$ and $\psi_{2\,\text{liquid}}$ respectively, we have:

$$RT\,.\ln p + \psi_1 = RT\,.\ln c + \pi\left(\frac{\partial V}{\partial n}\right)_{\pi_1 T} + \psi_2 \quad . \quad . \quad (9)$$

The derivate $\left(\frac{\partial V}{\partial n}\right)_{\pi_1 T}$ is proportional to Ångström's[12] "coefficient of dilatation by absorption"; it represents the dilatation of the liquid phase per mole absorbed gas.

Substituting the "Ostwald solubility" $\gamma = \frac{cRT}{p}$ we obtain

$$RT\,.\ln\frac{\gamma}{RT} = \psi_1 - \psi_2 - \pi\left(\frac{\partial V}{\partial n}\right)_{\pi_1 T} \quad . \quad . \quad . \quad (10)$$

which shows that γ is independent of p and represents therefore Henry's law. γ depends on π and T only, therefore

$$\left(\frac{\partial \ln\gamma}{\partial T}\right)_V = \left(\frac{\partial \ln\gamma}{\partial T}\right)_\pi + \left(\frac{\partial \ln\gamma}{\partial \pi}\right)_T\left(\frac{\partial\pi}{\partial T}\right)_V \quad . \quad . \quad (11)$$

Eliminate $\left(\frac{\partial \ln\gamma}{\partial\pi}\right)_T$ from the derivate of equation (10) by π and from equation (11) and express the "tension coefficient" $\left(\frac{\partial\pi}{\partial T}\right)_V$ as the ratio of thermal expansion (α) and compressibility (β) of the solvent (because these properties of the dilute solution may be regarded to a first approximation as identical with those of the solvent), we arrive finally at:

$$\frac{1}{\gamma}\left(\frac{\partial\gamma}{\partial T}\right)_V = \frac{1}{\gamma}\left(\frac{\partial\gamma}{\partial T}\right)_\pi - \frac{1}{RT}\left(\frac{\partial V}{\partial n}\right)_{\pi_1 T}\frac{\alpha}{\beta} \quad . \quad . \quad (12)$$

We calculated $\left(\frac{\partial\gamma_M}{\partial T}\right)_V$ for hydrogen in different solvents, using the $\left(\frac{\partial\gamma_M}{\partial T}\right)_\pi$ and $\left(\frac{\partial V}{\partial n}\right)_{\pi_1 T}$ measurements of Horiuti and the $\alpha_1\,\beta_1$ values given in the tables of Landolt-Börnstein. Table III. contains the result: the temperature coefficient of solubility of hydrogen would indeed be negative *at constant volume* of the solution, as predicted by Professor Polanyi. We were unable to calculate the same value on the least cohesive gas, on helium, because its Ångström[12] coefficients are not determined.

TABLE III.

Gas.	Solvent.	$\left(\frac{\partial \gamma_M}{\partial T}\right)_\pi$.	$\left(\frac{\partial \gamma_M}{\partial T}\right)_V$.
H_2	Ethyl ether	+ 0·11	− 0·14
H_2	Acetone	+ 0·07	− 0·03
H_2	Carbon tetrachloride	+ 0·07	− 0·10
H_2	Benzene	+ 0·06	− 0·11
H_2	Chlorobenzene	+ 0·05	− 0·07
N_2	Ethyl ether	+ 0·10	− 0·83

Solubility Measurements with Krypton.

The krypton contained about 5 per cent. xenon and 1 per cent. non-inert gases. We used the apparatus and method described by L. W. Winkler[13] but abstained from working in a thermostat and only immersed the glass bulb of about 250 c.c. in a water bath when dealing with solvents of high vapour pressure. The solvent in the bulb was evacuated through a side tube connected to a rotatory oil pump (with a liquid-air trap between) and we shook the bulb during the whole time of evacuation because this method was simpler than outgassing and evacuating the apparatus by boiling out the solvent as described by Winkler. The gas could be filled-in most conveniently through a capillary rubber tube attached to the gas pipette and bearing a short glass capillary at its other end. This was pushed above the mercury surface in the barometric tube and the capillary system was evacuated at the same time with the solvent. After the last traces of air disappeared, the side tube to the pump was closed and we

TABLE IV.—SOLUBILITY DATA.

Solvent.	Temp. C°.	Ostwald Solubility.
Ethyl alcohol, 95 per cent.	21	0·62
Ethyl alcohol, 97·5 per cent.	21	0·67
Cyclohexanol	22	0·40
Acetone (tech.)	19	0·83
Acetone (dried)	20	1·05
Benzene	22	0·97
Tetraline	24	0·49
Butylacetate (tech.)	20	0·85
Butylphthalate (tech.)	20	0·47
Tricresyl phosphate (tech.)	22	0·23
Acetic acid (glacial)	22	0·47
Glycerin	20	0·06
Chloroform	21	1·01
„	0	0·97
Bromoform	22	0·46
Carbon tetrachloride	21	1·31
„ „	0	1·20
20 per cent. $CaCl_2$ solution in water	22	0·04
Ar in chloroform	22	0·178

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[12] Ångström, *Wied. Ann.*, 1882, **15**, 297; 1888, **33**, 223; see also Horiuti.[7]

[13] L. W. Winkler, *Ber.*, 1891, **24**, 89.

could let in the gas through the capillary without throwing the mercury out of the barometric tube.

The measurements were originally intended to answer a technical question where accuracy of more than 10 per cent. was not desired. We estimate the error in the data to ± 5 per cent., though most of the determinations were reproduced to 2-3 per cent. We determined known solubilities to test the apparatus and found for the " Ostwald solubility " of :

Ar in water 0·036 at 22° C. instead of 0·034 and
N_2 in chloroform 0·128 at 22° C. instead of 0·130.

In addition to the new data for krypton we determined also the solubility of Ar in chloroform and we record the result because no better one is available.

Summary.

1. The empirical formula

$$\log \gamma_M = A + B \, . \, T_k$$

gives a very good approximation for the solubility of different gases in one solvent. The value of B varies but little from solvent to solvent; its constancy would indicate the validity of Just's law.

2. The temperature coefficient of solubility at constant pressure is positive for gases with T_k under 180° K., and negative for those with T_k above 180° K. The only solvent that does not agree to this rule is water. The temperature coefficient of solubility at constant volume is always negative.

3. The solubility of krypton was determined at room temperature in 16 solvents with an approximate maximal error of ± 5 per cent.

The author expresses his gratitude to Dr. I. Brody for much helpful advice and enlightening discursions.

THE NATURE OF POLISH.

By G. I. Finch.

Received 14th January, 1937.

A micrographical study of the surface changes produced by polishing led the late Sir George Beilby [1] to the view that polish resulted from a flowing of the material whereby the surface became coated with an amorphous layer, the so-called Beilby layer. His experiments demonstrated, in the clearest possible manner, that polishing does not consist in a levelling of the surface by a mere wearing away of projections, but that the polish layer is built up by a transfer of material from one part of the surface to another. On the other hand, it cannot be claimed that Beilby's results justify his further conclusions as to the supposed amorphous state of the flowing material and final polish layer.

A fresh impetus to the study of polish was afforded by Thomson and French [2] when they showed that a polished metallic surface grazed by an electron beam gave rise to a pattern of diffuse halos of a type consistent with diffraction by the liquid metal, a fact which was accordingly interpreted as testifying to the amorphous nature of the polish layer. This evidence, however, was shown to be inconclusive by Kirchner,[3] who found that thin metal films, formed in such a manner as greatly to limit the height to which crystals project above the region opaque to the electron beam, could give rise to halo patterns indistinguishable from those afforded by polished metal surfaces, although the sharp diffraction phenomena observed in transmission proved them to be crystalline. These results led Kirchner [4] to attribute the diffuse halo patterns afforded by mechanically polished metallic surfaces to a broadening of the diffractions as a result of poor resolving power due to a reduction, by the act of polishing, in the size of the crystals accessible to the beam. Thus, according to this view, polishing smooths the surface but leaves it crystalline, the halo pattern being formed by transmission through crystalline projections so unusually short as to afford but poor resolution.

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[1] G. Beilby, *Aggregation and Flow of Solids*, Macmillan, 1921.

[2] G. P. Thomson, *Proc. Roy. Soc.*, *A*, 1930, **128**, 649; R. C. French, *ibid.*, *A*, 1933, **140**, 637.

If the polish layer were amorphous, as supposed by Thomson, the beam should enter and leave through the same surface; unfortunately owing to the diffuseness of the halos, the inner potential refractive effect is too small to enable a decision to be made in favour of one or the other hypothesis. No less inconclusive are the experiments of Hopkins [5] and Lees [6] who, in attempting to measure the thickness of the polish layer, resorted to processes of progressive etching; their results will bear equally well either Kirchner's or Thomson's interpretation of the origin of the halo pattern from a polished metallic surface and its eventual displacement by sharp rings.

It may here be emphasised that the main facts are established beyond dispute, *i.e.*, that (i) amorphous surfaces like glass, silica and mercury, (ii) polished metallic, and (iii) certain crystalline metallic surfaces can all yield halo patterns. The fact that certain crystalline metallic surfaces can give rise to halo patterns appears, at present, to invalidate Thomson's interpretation of (ii) in terms of (i); but it is also clear that, in view of (i), Kirchner's interpretation of (ii) in terms of (iii) is equally untenable without further support. Thus, up to this point, the evidence can only be regarded as such as to leave in doubt the issue as to whether the polish layer is crystalline or amorphous.

So far, however, we have omitted mention of the fresh light, apparently overlooked by Kirchner,[4] which Finch, Quarrell and Roebuck [7] brought to bear on the subject when they found that the polish layer on metals has the property, characteristic of a liquid and not exhibited by the corresponding crystalline surface, of dissolving to saturation crystals of a foreign metal at room temperature. It was mainly this evidence which, although necessarily obtained by the method of electron diffraction, falls into quite a different class to that brought forward by Kirchner and Thomson, and which has been largely instrumental in leading to the present wide acceptance of the amorphous nature of the metallic Beilby layer. The demonstration of the remarkable solvent powers of the metallic polish layer makes it difficult to resist the conclusion that the layer is amorphous, *i.e.*, glass-like. The obvious corollary, *i.e.*, that the surface flow is likewise one of material rendered amorphous by the action of polishing, receives independent support from Bowden and Ridler's [8] experiments, which also seem to have escaped Kirchner's notice, by which it was shown that the mean temperature of the polish layer during its formation quickly rose to a limit equal to the melting-point of the metal and independent of any further increase in the vigour of the polishing action. Considered in conjunction with Beilby's demonstration of surface flow, particularly by the exposure by etching of scratches eliminated by polishing, this striking result strongly suggests that the flow occurring during polishing must be one of liquefied, *i.e.*, amorphous material, rather than of crystalline detritus.

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[3] F. Kirchner, *Trans. Faraday Soc.*, 1935, **31**, 1114.

[4] F. Kirchner, *Ann. d. Physik*, 1937, **28**, 21.

[5] H. G. Hopkins, *Trans. Faraday Soc.*, 1935, **31**, 1095.

[6] C. S. Lees, *ibid.*, 1102.

[7] G. I. Finch, A. G. Quarrell and J. S. Roebuck, *Proc. Roy. Soc., A*, 1934, **45**, 676.

Finch, Quarrell and Wilman [9] have shown that, whilst a hand-polished steel surface gave a sharp-ringed α-iron pattern after a single light stroke with No. 000 emery paper, several such abrasions were necessary to produce this result when similar steel surfaces had previously been subjected as component surfaces in an internal combustion engine to the vigorous polishing action of a prolonged period of "running-in." These facts suggest that the growth of the Beilby layer increases with the vigour and time of polishing; they do not seem to fit in with Kirchner's view, for otherwise the "run-in" surface should have responded to scratching as easily as did the hand-polished specimen.

In the light of these facts and considerations, it may be concluded that the metallic Beilby layer is amorphous, and is formed by a surface flow of amorphous, vitreous-like or liquid material produced by the action of polishing. Furthermore, it now seems justifiable to regard the halo pattern obtained from a mechanically worked, *i.e.*, polished, burnished or hammered metallic surface, as evidence of an amorphous layer.

It is now well known that natural and cleavage faces of single crystals yield at grazing incidence characteristic Kikuchi line patterns, though such faces are generally relatively rough, and are indeed seldom, if ever, microscopically smooth. When Germer [10] found that the quite exceptionally smooth and beautifully developed basal planes of single crystals of silicon carbide only gave diffuse rings, he attributed this halo pattern to the extreme smoothness of the crystals, and inclined further to the view that a gas layer might possibly also play a contributory rôle when adsorbed on such a smooth surface. The typical Kikuchi line pattern yielded after treatment with fused caustic potash was attributed by Germer to a roughening of the carbide surface by etching. This seems a remarkable conclusion, because it is now a matter of general experience that roughening, whether by chemical or mechanical means, of a natural or cleavage single crystal face leads to replacement of the true reflection pattern of Kikuchi lines and refractive displacement of pattern features by that kind of "reflection" pattern of cross-grating spots which Thomson [11] has shown to be due in effect to transmission through crystalline projections integral with the main body of the crystal. As a result of a series of simple experiments, however, Finch and Wilman [12] were

[8] F. P. Bowden and K. E. W. Ridler, *Proc. Roy. Soc., A*, 1936, **154**, 640.

[9] G. I. Finch, A. G. Quarrell and H. Wilman, *Trans. Faraday Soc.*, 1935, **31**, 1051.

[10] L. H. Germer, *Physical Review*, 1936, **49**, 163.

[11] G. P. Thomson, *Proc. Roy. Soc., A*, 1931, **133**, 1.

[12] G. I. Finch and H. Wilman, *Trans. Faraday Soc.*, 1937, **33**, 337.

able to put a very different interpretation upon Germer's results Thus, like Germer, they invariably obtained halo patterns from undamaged single crystal surfaces of silicon carbide; but it was also found that after gentle rubbing with a fine abrasive (moist rouge and alumina) softer than the carbide but harder than silica, or after an etching treatment (hydrofluoric acid or caustic potash solution) capable of attacking silica but not the carbide, and none of which treatments had any visible effect on either the appearance or smoothness of the surfaces, the crystals afforded remarkably clear and brilliant Kikuchi line patterns typical of reflection from a single crystal surface. Finally, progressive oxidation of such carbide crystal surfaces led to the formation of composite halo and single crystal patterns, in which the Kikuchi lines showed more or less faintly through the diffuse background of general scattering which always accompanies the halo pattern until, after sufficient oxidation, the halo pattern prevailed alone. These results show that the halo patterns yielded by untreated silicon carbide crystals are due to an amorphous skin, probably of silica, formed by surface oxidation, no doubt on cooling of the charge in the course of manufacture.

It will be recalled that in many of his experiments Beilby had observed the phenomenon of surface flow on non-metals, such as calcite, and had, in fact, come to the conclusion that the polish layer is amorphous, not only on metals, but also on non-metals. Indeed, the phenomenon of surface flow is particularly easily demonstrated with calcite. As pointed out above, however, this fact does not justify Beilby's further conclusions as to the state of the surface flow and final polish layer. Thus, Raether[13] and Hopkins[14] have shown conclusively that the polish layer on the calcite cleavage face is of single crystal structure integral with that of the underlying crystal. Since the occurrence of surface flow proves that the polishing of calcite is not simply a matter of attrition, the question still remains open as to whether the structure of the final polish layer on the calcite cleavage face is due to a recrystallisation of surface-flowed amorphous material in orientation with the substrate, or to a similarly ordered deposition of crystalline fragments or sheets transferred from one part of the surface to another. The following experiments enable us to come to a decision.

The cemented calcite prism-pairs of a Zeiss polariser and analyser were separated and their protective cover glasses detached by soaking in 95 per cent. alcohol. The four end and four junction faces thus exposed were seen to be highly polished. These polariser prisms are cut in such a manner that each square-shaped end face is a cleavage plane, and is intersected roughly diagonally by the other two cleavage plane directions. The junction face, however, passes through an edge of the end face, and is approximately perpendicular to it. Thus the junction face is steeply inclined to all three cleavage plane directions. The polariser end faces gave single crystal patterns of which Fig. 1 is characteristic, but the corresponding junction faces yielded halo patterns. The analyser prisms, however, are cut so as to form together a square-ended rectangular parallelepiped with the junction faces forming a diagonal plane passing through the edge of, and enclosing an angle of 71° with, each end face. The two side faces normal to the junction face are cleavage plane directions. The other two cleavage planes intersect the sides of the prism in lines which both make angles of about 140°, but in opposite senses, with the long edge

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[13] H. Raether, *Z. Physik*, 1933, **86**, 82.
[14] H. G. Hopkins, *Phil. Mag.*, 1936, **21**, 820.

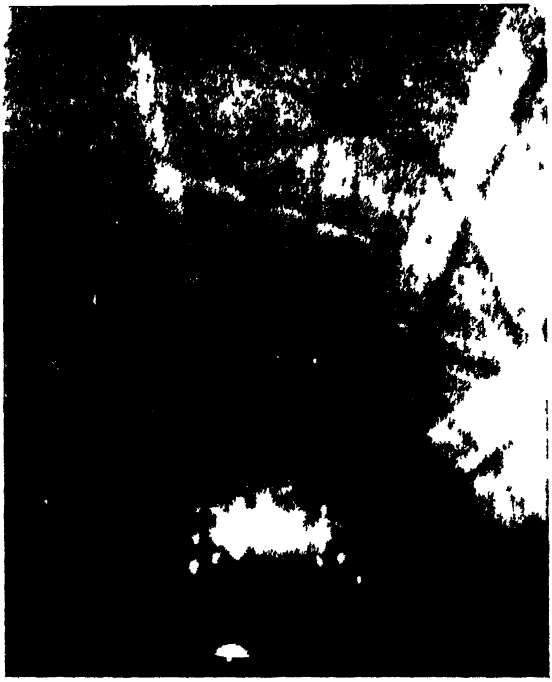

FIG. 1.—Pattern from polished end face of a Zeiss Nicol prism.

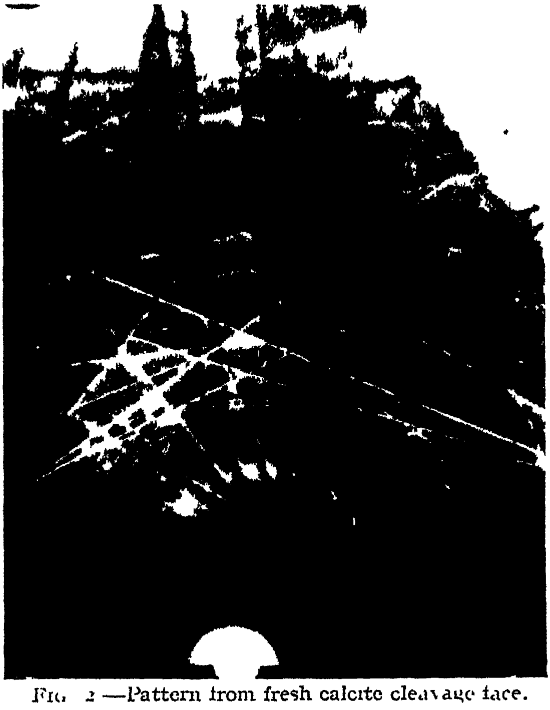

FIG. 2.—Pattern from fresh calcite cleavage face.

of the prism base. Thus the analyser end and junction faces are considerably inclined to all the cleavage plane directions, though not to the same extent as are the polariser junction faces. The analyser end and junction faces gave relatively ill-defined electron diffraction patterns consisting of many broadened spots, faint diffuse haloes and faint signs of Kikuchi lines.

To confirm these observations a natural rhomb of calcite was cut in such a manner that the cut face corresponded to the junction face of the polariser prism. The cut face and a cleavage face of about the same area were ground on fine emery and polished, using rouge on a rotating disc of pitch, the two surfaces being treated in an exactly similar manner. It was again found that the polished cleavage face gave a single crystal pattern similar to Fig. 1, whereas the polished cut face gave a halo pattern. After a brief etching with $n/10$ hydrochloric acid, which exposed many coarse grinding scratches, these faces, ten in all, yielded single crystal patterns similar to Fig. 1, but with a somewhat stronger and more extended primary diffraction spot pattern. Polishing with moist rouge on a rotating soft pitch table obliterated the scratches exposed by etching and, whilst all faces in cleavage directions continued to yield patterns similar to Fig. 1, the polariser junction faces now gave rise to halo patterns which, in the case of the analyser prism faces were accompanied by diffuse diffraction spots and traces of Kikuchi lines showing faintly through the intense background which always accompanies the halo pattern. One polariser prism was then truncated by cleaving in such a manner as to reduce the area of the junction face to that of the adjoining end face. Judging from the definition of the Kikuchi lines and limited extent of the primary spot pattern, Fig. 2, obtained from the fresh cleavage face, is characteristic of an exceptionally smooth face of a well-developed crystal. Etching again revealed typical grinding scratches on the end and junction faces, but the cleaved face, though slightly roughened, showed no such signs of surface flow. The corresponding patterns were all similar in type to Fig. 1. All three faces were then polished, with the result that, though the end and cleavage faces continued to afford patterns like Fig. 1, the junction face gave only halos, although the vigour of polishing to which it had been subjected must have been similar to that of the end face which was of the same area and shape.

The final series of experiments consisted in a preliminary heating of the truncated prism with its three polished faces in an air-carbon dioxide atmosphere to about 250° during three-quarter hours followed, after examination in the electron diffraction camera, by two hours at about 500°. After the first stage of this treatment which had no visible effect on any of the polished faces, the junction face gave a composite pattern consisting of diffuse primary spots and Kikuchi lines showing faintly through the halo pattern and its associated background, similar in type to that afforded by a silicon carbide crystal surface coated with a thin amorphous silica film.[15] After the second period of heating it was found, however, that the halo pattern had vanished, to give way to a single crystal pattern similar in type to those yielded by the polished end and cleavage faces both before and after heating.

The revealing of recognised scratches by etching of the polished faces confirms that a surface flow occurs during the polishing of calcite. The fact that the polished junction faces yielded halo patterns enables the conclusion to be drawn that polishing results in a surface flow of amorphous material to form a vitreous-like Beilby layer devoid of ordered crystal structure. The effect of heating in causing the halo pattern from the polished polariser junction face gradually to give way to an emerging pattern, characteristic of single crystal structure, justifies the conclusion that the single crystal type of polish layer formed on the end cleavage faces of the calcite polariser prism results from a crystallisation of the amorphous flowed material, induced and governed in its orientation by the underlying single crystal, recrystallisation proceeding outwards from this substrate through the Beilby layer. The end faces of the polariser prisms are cleavage planes or nearly so, but the junction faces are steeply inclined to all cleavage directions, and intermediate between these lie the analyser prism faces. It seems that the substrate effect in promoting recrystallisation of calcite, which has been caused to flow in an amorphous state by polishing, is strong in the cleavage plane and neighbouring directions, but sluggish elsewhere.

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[15] G. I. Finch and H. Wilman, *Trans. Faraday Soc.*, 1937, **33**, 337, Fig. 2.

Summary.

Evidence is reviewed upon which was based the idea of the vitreous-like nature of polish. It is pointed out that the phenomenon of surface flow leaves open the question as to the state, whether amorphous or crystalline, of the flowing material or final polish layer. The fact that metallic polish yields halo patterns by electron diffraction is also inconclusive, because not only amorphous, but also certain crystalline metal films behave similarly.

The ability, not exhibited by the corresponding crystalline surface, of metallic polish to dissolve metal crystals strongly supports the view of the amorphous state of both surface flow and polish, as does also the fact that the temperature of flow is limited by the melting-point of the metal.

It has been shown experimentally that polishing results in flow on calcite single crystal surfaces, and that the polish layer is crystalline and integral in structure with the underlying crystal when the surface is a cleavage plane or is close in its direction to those of such a plane; but affords, on the other hand, halo patterns when the polished surface is steeply inclined to all cleavage planes. Heating leads to the gradual emergence of a single crystal pattern through, and the eventual replacement of, the halo pattern. In view of the fact that the gradual formation of an amorphous skin on a silicon carbide crystal by a superficial oxidation is accompanied by the degeneration of the characteristic single crystal pattern into one of the halo type and *vice versa* on removal of the skin, it is concluded that the polish layer on a calcite surface remote in direction from any cleavage plane is amorphous. It is further concluded that surface flow is one of vitreous or liquid-like material, and that the crystalline structure of the polish layer on the calcite cleavage plane is due to recrystallisation of such flowed material under the influence of the underlying substrate crystal; an influence which, however, is weak in surfaces steeply inclined to the directions of cleavage.

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NOTE ON THE USE OF SODIUM DIETHYLDITHIOCARBAMATE FOR DETECTING THE SOLUBILITY CORROSION OF METALS.

By W. R. G. Atkins, Sc.D., F.R.S.

Received 11*th February*, 1937.

In biological work it is often of importance to detect whether a metal gives off poisonous ions, such as those of copper or zinc. The dialkyldithiocarbamates were introduced by Delépine[1] as reagents for copper and iron. Subsequently Callan and Henderson[2] showed that sodium diethyldithiocarbamate was the most sensitive reagent for copper and described the reactions with a number of other metals. Atkins[3] has used this reagent for the turbidimetric estimation of zinc. It serves well for the study of corrosion in a number of cases, since the colour reactions or precipitates characteristic of many metals are given when a 0·1 per cent. solution of this salt is added to the liquid to be studied, which should be neutral or faintly alkaline. The metal is then immersed. Within a short time, to be measured in seconds in some cases, visible effects are produced. In others, such as with highly resistant bronzes, or combinations, such as zinc and copper, a portion of the solution is extracted with one-tenth or one-twentieth of its volume of chloroform or carbon tetrachloride ; by this means a colour due to the copper diethyldithiocarbamate may be revealed or the definite absence of even so slight a trace of the metal may be proved. Similar results are obtained by adding the reagent after a given time, but to study almost instantaneous and local effects it is necessary to start with the reagent present.

Changes involving the solution of metals may be studied colorimetrically or turbidimetrically, by the aid of dithiocarbamate. With a brass for example, when immersed in seawater, the first precipitate was a white one due to zinc alone, but this was soon followed by a more rapid coloration—due to copper—than is found with copper alone. It is possible to estimate the zinc turbidimetrically in the presence of the golden colour of the copper compound by observing both the pure zinc standard and the unknown, through an orange coloured glass. The OG2 of Schott (Jena), which is a close match to the colour of the copper salt, is suitable for this. For estimating copper alone the zinc precipitate may be filtered off. Precipitates of zinc and lead may be distinguished by the fact that the former dissolves easily in ammonia whereas the lead is insoluble in both ammonia and very dilute acids. The behaviour of ordinary yellow 2 : 1 brass in sea water is quite understandable in the light of Rawdon's work.[4] After the initial white turbidity, due to zinc going into solution from a surface layer, the zinc rich β constituent of the brass dissolves yielding both metals.

Table I. gives the results obtained by making use of sodium diethylthiocarbamate in the study of corrosion. One is struck by the great

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[1] Delépine, *Bull. Soc. Chim.* (iv.), 1908, **3**, 652 ; *Abstr. J. Chem. Soc.*, 1908, ii., 633.

[2] Callan and Henderson, *Analyst*, 1929, **54**, 650.

[3] Atkins, *ibid.*, 1935, **60**, 400.

[4] H. S. Rawdon, U.S.A. Bureau of Standards, Technologic Paper No. 103, 1917.

TABLE I.—CORROSION TESTS OF METALS IN SEA WATER, USING SODIUM DIETHYLDITHIOCARBAMATE AS DETECTOR.

Metals.	Result.
Zinc, sheet.	Very rapid action, white turbidity in a few seconds.
Zinc, granulated arsenic free	Very rapid action, white turbidity in a few seconds.
Copper	Action slower, golden brown colour and ppt. in a few minutes.
Copper + zinc, clamped.	Very rapid action, white turbidity.[5]
Copper and zinc, wax between.	Each metal acted much as if alone.
Steel.	Very rapid action, dark brown colour and ppt.[6]
Tin, granulated.	No action, save at two small points after some while.
Brass.	At first white zinc ppt. only, then more copper ppt. than from copper alone.
Gun metal, dull weathered.	No trace after 4 hours using extraction test; very slight amount of copper detected by extraction after 24 hours.
Gun metal, polished with emery.	Slight attack, demonstrated by extraction after 10 min.
Gun metal, polished + silver.	Action visible in a few minutes, copper given off. Confirmed by extraction. Silver not attacked but darkened at one spot.
Gun metal, dull + silver.	No appreciable action beyond the trace shown by the alloy alone.
Tin + copper.	Slow action, white ppt. on tin only.
Lead, fresh surface.	Very slow, very slight action, white film adhering.[7]
Lead + copper.	No action on copper, slight action on lead, a little more than with lead alone.
Silver + copper.	Copper more attacked than when alone, silver not attacked.

rapidity of the reaction and the simplicity of the tests; without a potentiometer, or any apparatus beyond glass vessels, one can arrange various elements in the order of the electrochemical series. Rapid preliminary information can also be obtained concerning the corrosion of many alloys, and the experiments are well suited for demonstration to classes. One point shown very clearly is the remarkable difference between the action of fresh and sea water upon lead—see footnote to Table.

Summary.

Sodium diethyldithiocarbamate serves well for the study of the solubility corrosion of metals in a number of cases and preliminary surveys and quantitative studies may be made with it, particularly when dealing with copper, iron, lead and zinc.

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Plymouth.

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[5] Copper tested for by extraction with chloroform after three days, no trace found.

[6] A stainless steel mesh, action scarcely perceptible in seven weeks.

[7] The action is rapid in distilled water.

ON THE THEORY OF DIFFUSION IN FAST STREAMING VAPOURS.*

BY D. MACGILLAVRY.†

Received 30*th November*, 1936.

When studying the diffusion of hydrogen in streaming mercury vapour, with the end of concentrating the isotopes of hydrogen, it was felt that a further development of the theory was needed. This more complete theory is now presented.

As Hertz[1] has already pointed out, the motion of a diffusing pure gas in a streaming medium is made up of two parts. The gas present at each point is swept away with the velocity of the medium at that point. Superposed on this is a diffusion along the density gradient:

$$\bar{\imath} = \rho\bar{v} - \delta \operatorname{grad} \rho, \quad . \quad . \quad . \quad . \quad (1)$$

where $\bar{\imath}$, ρ and δ are respectively the flow, the density and the interdiffusion constant of the gas and the medium, and $\bar{v}$ is the medium velocity.

Stationary states of diffusion only will be considered. In such cases the amount of gas at any point does not vary with time; hence

$$\operatorname{div} \bar{\imath} = 0. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If there is no moving medium, then $\bar{v} = 0$, from which follows

$$\operatorname{div} \operatorname{grad} \rho = 0. \quad . \quad . \quad . \quad . \quad (3)$$

The diffusion constant has dropped out of this last equation. Consequently, when a stationary state of diffusion in a medium at rest has been obtained, then the density distribution is no more dependent upon the diffusion constant, and the ratio of the partial pressures of a diffusing mixture would be constant everywhere and equal to the original ratio. The flow, however, would still be proportional to the diffusion constant according to equation (1), so long as a distribution gradient is existent. The ratio of the flows for the components of a mixture would then differ from the ratio of the partial pressures. Such processes, often called effusion, are exemplified in the effusion from a narrow opening and the diffusion through porous clay tubes.

If now the medium is moving, the boundary conditions must be taken in consideration. Hereafter we assume that the medium flows with constant velocity $v = v_z$ in the direction of the positive z-axis, hence

$$\operatorname{div} \bar{v} = 0,$$

and consequently

$$\operatorname{div} \operatorname{grad} \rho = a\frac{\partial \rho}{\partial z} \quad \left(a = \frac{v_z}{\delta}\right). \quad . \quad . \quad . \quad (4)$$

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* This article is based on the thesis presented to the Faculty of the Graduate School of Columbia University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June 1933.

† Holder of a Columbia University Fellowship during the academic year 1931-1932, Ramsay Memorial Fellow at the University of Cambridge.

[1] G. Hertz, *Physik. Z.*, 1922, **23**, 433; *Proc. Acad. Sci., Amsterdam*, 1922, **25**, 434.

Hertz solved the equation for two simple sets of boundary conditions. In the case of linear diffusion against the streaming medium we have

$$\frac{\partial^2 \rho}{\partial z^2} = a\frac{\partial \rho}{\partial z}, \quad . \quad . \quad . \quad . \quad . \quad (5a)$$

and we may put

$$\left.\begin{array}{ll} \rho = \rho & (z = 0) \\ \rho = 0 & (z = -m) \end{array}\right\} \quad . \quad . \quad . \quad . \quad (5b)$$

The solution is

$$\left.\begin{array}{l} \rho = P(e^{az} - e^{-am}) \\ i = -vPe^{-am} \end{array}\right\}(P \sim \rho^* \text{ for large } m) \quad . \quad . \quad (5c)$$

Hertz' second example is of diffusion in three dimensions with very simple boundary conditions. For three-dimensional diffusion equation (4) takes the form

$$\frac{\partial^2 \rho}{\partial x^2} + \frac{\partial^2 \rho}{\partial y^2} + \frac{\partial^2 \rho}{\partial z^2} = a\frac{\partial \rho}{\partial z}. \quad . \quad . \quad . \quad (6a)$$

The point of entry of the diffusing gas being taken as the origin of the co-ordinate system and the boundary condition being defined by

$$\rho = 0 \quad (s = \infty), \quad . \quad . \quad . \quad . \quad (6b)$$

where s is the radius vector, we obtain

$$\rho = \frac{C}{s}\exp\left\{-\frac{a}{2}(s - z)\right\} \quad . \quad . \quad . \quad (6c)$$

The exponential drop off in density expressed by both of these solutions may be taken as the general characteristic of this problem. The first case of linear diffusion against the velocity of the streaming medium can have been realised in practice only with difficulty, since the motion readily sets up eddy currents, especially at the point where the diffusing gas is introduced. We should not, therefore, expect the method applied in this way to be effective for the separation of the hydrogen isotopes.

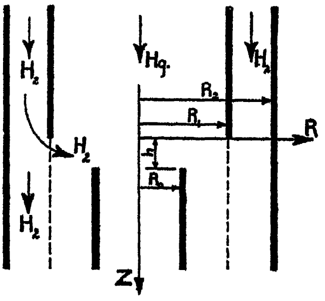

FIG. 1.

A new diffusion chamber was, therefore, designed for the concentration of the hydrogen isotopes and used successfully. The hydrogen isotopes were diffused into mercury vapour used as the fast streaming medium. The complete diffuser and the technical details of the operation are given in the dissertation. The part of the diffuser where the actual diffusion takes place is sketched in Fig. 1.

The second case comes nearer to the conditions existing in the new diffuser. Here again, the region where diffusion takes place has cylindrical symmetry.

The mercury vapour enters through the nozzle (radius R_1) and upon leaving the nozzle forms a cylindrical stream of the same radius within which, unless otherwise stated, the mercury is at all times confined; the velocity distribution is uniform and the lines of flow are parallel. Consider first the case when an atmosphere of a pure gas, say of $H^1{}_2$, surrounds the mercury jet. In order to prevent turbulent flow where the gases come into contact with each other this gas must flow through the diffuser with the same velocity as the mercury. A tube is placed in the axis of the mercury stream at a small distance h away from the nozzle opening. The diffusion of hydrogen into the mercury stream is superimposed upon the uniform motion with constant velocity. Part of the mercury and of the diffused hydrogen flow off through the narrow collecting tube. The rate of diffusion of the hydrogen is small in comparison with the main flow velocity of the mercury, so that its partial pressure within the collector remains less than 10^{-4} of the total pressure. The partial pressure of the mercury remains practically equal to the total pressure, which is assumed to be constant in the diffusion chamber. The mercury, therefore, does not spread, thus justifying our assumption that the lines of flow remain parallel. The radial inter-diffusion is a second order phenomenon as compared with the fast flow downward.

It is useful to observe that i is independent of the total pressure, because the density is directly proportional to the pressure, while the diffusion constant and the velocity v_z are inversely proportional to the pressure, so long as the amount of liquid mercury distilled per minute is kept constant. For these reasons also a in equations (4) is independent of the pressure.

In order to set up boundary conditions, suitable for the theoretical discussion of the new diffuser, we observe that no hydrogen can flow through the glass wall of the nozzle:

$$i_r = -\delta\frac{\partial\rho}{\partial r} = 0, \quad (z < 0, \ r = R_1) \quad . \quad . \quad . \quad (7)$$

furthermore, when the steady state of diffusion has been reached, the total flow of hydrogen across the nozzle opening is zero:

$$\int_0^{R_1} 2\pi r i_z dr = 0, \quad (z = 0), \quad . \quad . \quad . \quad (8)$$

finally, it may be assumed that the density is constant along the cylinder surface, where the hydrogen and mercury come into contact:

$$\rho = \tfrac{1}{2}\rho^*, \quad (z > 0, \ r = R_1). \quad . \quad . \quad . \quad (9)$$

Equations (7), (8) and (9) are the boundary conditions. These together with the differential equation (4), which rewritten in cylindrical co-ordinates takes the form

$$\frac{\partial^2\rho}{\partial r^2} + \frac{1}{r}\frac{\partial\rho}{\partial r} - \frac{\partial^2\rho}{\partial z^2} = a\frac{\partial\rho}{\partial z}, \quad . \quad . \quad . \quad (10)$$

determine the density distribution of the hydrogen in the mercury stream.

Murray has made an analysis of this system of equations, which can be applied even when condition (9) is replaced by the arbitrary distribution

$$\rho = f(z), \quad (z > 0, \ r = R_1). \quad . \quad . \quad . \quad (9a)$$

The general solution, unfortunately, does not permit rapid numerical calculations. Since the complications arise from the condition (9), we have sought simpler boundary conditions which can be justified from physical considerations.

Now, if the region of diffusion studied can be extended over the whole width of the chamber, the condition that there is no flow of hydrogen through the outside wall is mathematically much more convenient. The density of hydrogen across the nozzle is zero, moreover, if back diffusion in the Z-direction can be neglected. The physical problem can then be restated as follows. Consider a thin cross-section of gas in the chamber at the height of the nozzle. At distances from the axis smaller than R_1 the gas is pure mercury, at greater distances it is pure hydrogen. The hydrogen and mercury interdiffuse while this whole cross-section moves downward with velocity v_z, but they do not leave this section. The gases become completely mixed at infinite distance. The equation for this process is easily seen to be

$$2\pi r\frac{\partial\rho}{\partial t} = \frac{\partial}{\partial r}\left(2\pi r\delta\frac{\partial\rho}{\partial r}\right). \quad . \quad . \quad . \quad (11)$$

Since the distance travelled downward is given by $z = v_z t$, this becomes:

$$\frac{\partial^2\rho}{\partial r^2} + \frac{1}{r}\frac{\partial\rho}{\partial r} - a\frac{\partial\rho}{\partial z} = 0. \quad . \quad . \quad . \quad (12)$$

The boundary condition for zero density of hydrogen across the nozzle opening is

$$\left.\begin{array}{ll} \rho = 0 & (z = 0, \quad 0 < r < R_1) \\ \rho = \rho^* & (z = 0, \ R_1 < r < R_2) \end{array}\right\} \quad . \quad . \quad (13a)$$

and for impermeability of the diffuser outer wall the boundary condition is

$$\left.\frac{\partial\rho}{\partial r} = 0 \quad (z > 0, \ r = R_2)\right\}. \quad . \quad . \quad . \quad (13b)$$

The solution[2] for the density distribution satisfying equations (12), (13a) and (13b) is:

$$\frac{\rho}{\rho^*} = \left(1 - \frac{R_1^2}{R_2^2}\right) - 2\sum\frac{R_1}{R_2}\frac{\mathcal{J}_1\left(\frac{R_1}{R_2}\lambda_n\right)}{\lambda_n\mathcal{J}_0^2(\lambda_n)}\mathcal{J}_0\left(\frac{r}{R_2}\lambda_n\right)\exp\left(-\frac{\lambda_n^2}{R_2^2}\frac{z}{a}\right), \quad (14)$$

where $\mathcal{J}_n$ is the nth Bessel function of the first kind and the λ_n's are the roots of $\mathcal{J}_1(\lambda_n) = 0$.

The density distribution depends upon the dimensions of the diffuser, the velocity of flow of the mercury vapour v_z and upon the interdiffusion constant. Thus the quantity a in the equations is characteristic for each individual gas.

The above solution is helpful for the study of diffusing gas mixtures, when the individual solutions can be superimposed. The assumption that each kind of molecule diffuses independently of the other kinds present seems to be justifiable for those regions where the concentrations of the diffusing gases are very small. Their presence scarcely alters the properties and the flow of the medium in which the diffusion takes place.

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[2] J. S. Townsend, *Electricity in Gases*, p. 164.

Each particular gas retains its characteristic a. We may assume that the individual solutions (14) can be used for the region of z where the lines of flow do not diverge.

When a gas mixture is diffusing, a partial concentration is obtained by collecting the gases which diffuse into the collecting tube. In order to determine the efficiency of the diffuser we must calculate these amounts for each gas separately. For the flow through a disc with radius R_0 and at a distance h from the nozzle we derive

$$f = \frac{F}{p^k} = \int_0^{R_0} 2\pi r v \frac{p}{p^*}\bigg|_{z=h} dr$$

$$= \pi v \left\{ \left(1 - \frac{R_1^2}{R_2^2}\right) R_0^2 - 4R_0R_1 \sum \frac{\mathcal{J}_1\left(\frac{R_0}{R_2}\lambda_n\right) \mathcal{J}_1\left(\frac{R_1}{R_2}\lambda_n\right)}{\lambda_n^2 \mathcal{J}_0^2(\lambda_n)} \exp\left(-\frac{\lambda_n^2}{R_2^2}\frac{h}{a}\right) \right\} \quad (15)$$

Referring to equation (1) it should be noted that, since v_z (and consequently a) has a very large value with respect to δ, the back diffusion is actually very small, except near the ring of (artificial) discontinuity at the edge of the nozzle, where $\partial p/\partial z$ becomes abnormally large. Therefore, the zero flow across the nozzle, represented by equation (8), is in reality the result of a negative flow very close to the nozzle edge and a positive flow nearer to the centre. Equations (14) and (15) are good approximations at most points, but break down at very small values of z and h.

The implicit assumption that the interdiffusion constant for a pure gas remains the same throughout the whole region may seem more doubtful. The concentration of hydrogen is very small at the centre and very large at the outside. The constant, therefore, differs in the two cases and generally depends upon the composition. The theoretical limiting ratio [3] is

$$\frac{\delta_{v_1=0}}{\delta_{v_2=0}} = \frac{1 + \dfrac{m_2^2}{12m_2^2 + 16m_1m_2 + 30m_1^2}}{1 + \dfrac{m_1^2}{12m_1^2 + 16m_1m_2 + 30m_2^2}},$$

which is 1·08 for both isotopic molecules H^1_2 and H^1H^2 diffusing in mercury. It is unlikely that the simplification introduces large errors.

Equations (14) and (15) are still too cumbersome; a rapid approximation should be found to serve as a guide for the construction of the best diffuser. Clearly the axis of the cylinder takes no part in the diffusion process for small values of z, so we may replace the coaxial cylinders by parallel planes and study the diffusion in the X-direction perpendicular to the planes (Fig. 2).

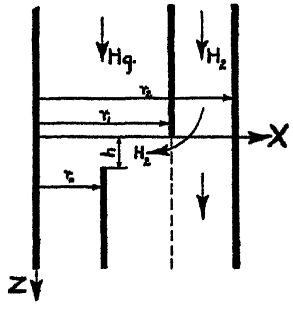

FIG. 2.

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[3] J. H. Jeans, *The Dynamical Theory of Gases*, 3rd ed., p. 319

The differential equation now takes the form

$$\frac{\partial^2 \rho}{\partial x^2} + \frac{\partial^2 \rho}{\partial z^2} - a\frac{\partial \rho}{\partial z} = 0, \quad . \quad . \quad . \quad . \quad . \quad (16)$$

which, neglecting the back diffusion as before, becomes :

$$\frac{\partial^2 \rho}{\partial x^2} - a\frac{\partial \rho}{\partial z} = 0. \quad . \quad . \quad . \quad . \quad . \quad (17)$$

The analogous boundary conditions are

$$\left.\begin{array}{ll} \rho = 0 & (z = 0,\ 0 < x < r_1) \\ \rho = \rho^* & (z = 0,\ r_1 < x < r_2) \end{array}\right\} \quad . \quad . \quad . \quad (18a)$$

and

$$\left.\begin{array}{ll} \dfrac{\partial \rho}{\partial x} = 0 & (z > 0,\ x = 0) \\ \dfrac{\partial \rho}{\partial x} = 0 & (z > 0,\ x = r_2) \end{array}\right\} \quad . \quad . \quad . \quad . \quad (18b)$$

The solutions for the density and the flow are :

$$\frac{\rho}{\rho^*} = \left(1 - \frac{r_1}{r_2}\right) - 2\sum \frac{1}{n\pi} \sin n\pi\frac{r_1}{r_2} \cos n\pi\frac{x}{r_2} \exp\left(-\frac{n^2\pi^2}{r_2^2}\frac{z}{a}\right), \quad (19)$$

$$f = \frac{F}{\rho^*} = vL\left\{\left(1 - \frac{r_1}{r_2}\right)r_0 - 2r_2\sum\frac{1}{n^2\pi^2}\sin n\pi\frac{r_0}{r_2}\sin n\pi\frac{r_1}{r_2}\exp\left(-\frac{n^2\pi^2}{r_2^2}\frac{h}{a}\right)\right\}, \quad (20)$$

where $L = 2\pi r_0$.

The efficiency α of any diffusion process is given by the ratio of the amounts collected divided by the ratio of the original densities. Hence :

$$\alpha = \frac{F_1}{F_2} : \frac{\rho_1^*}{\rho_2^*} = \frac{f_1}{f_2}. \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Equation (20) was used for most of the numerical calculations. The practical application of the theory developed here will be given in another article.*

Recently Hertz [4] described a diffuser of similar design, to which this theory would apply, if the mercury stream did not spread. Assuming this, Barwich [5] has derived an approximate formula for the fractionation ratio, which in our notation reads

$$\alpha = \frac{\delta_1}{\delta_2} \exp\left\{\frac{a_2 - a_1}{2}(R_1 - R_0 - h)\right\}.$$

This formula is evidently a rough approximation, holding only when $h \ll R_1 - R_0$. It reduces, for the case $h = 0$, omitting the factor δ_1/δ_2, to the approximation

$$\alpha = \exp\left\{\frac{a_2 - a_1}{2}(R_1 - R_0)\right\},$$

mentioned in the author's dissertation.

These expressions agree with the conclusion, derived from Murray's general theory, that the fractionation ratio increases quasi-exponentially with the thickness of the cylindrical mercury layer through which the

* Which will appear shortly in *Rec. trav. chim.*

[4] G. Hertz., *Z. Physik*, 1934, **91**, 810.

[5] H. Barwich, *ibid.*, 1936, **100**, 166.

gases must diffuse before reaching the collecting tube. We have investigated in our experiments primarily the dependence of the fractionation ratio on the dimensions of the apparatus and on the linear velocity of the mercury vapour. For the description of these experiments the reader is referred to the author's dissertation.

In so far as the new Hertz diffuser acted simultaneously as a circulating pump, the operating conditions must have been such that the mercury stream spread a great deal. Barwich studied in greater detail the dependence of the fractionation ratio on the diffusion constants of various gas mixtures and on the operating conditions, *i.e.*, the heating and the gas pressure. The heating determines the rate of mercury flow, which we shall assume to be proportional to the linear flow of the vapour, neglecting the spreading.

The observation by Barwich of two maxima of the fractionation ratio on increasing the heating may be explained, in our view, by taking into account the two possibilities of spreading and of turbulent flow.* Since the mercury vapour is blown into a stagnant gas atmosphere, and is thus used to circulate both fractions, turbulent flow is very probably caused in the layer of contact as soon as the mercury velocity increases above a critical value. An initial increase in the fractionation ratio is thus suddenly off-set and after a first maximum a decrease occurs. By increasing the heating more and more the mercury stream will tend to spread, while the centre of the stream still possesses streamline flow. Conditions were, apparently, such that the fractionation ratio could increase again, to reach a second maximum. The region of turbulent flow is pressed aside. When the mercury velocity is yet more increased, the opportunities for turbulence become so great that turbulence sets in also in the centre of the mercury stream, and the separation efficiency falls off sharply. When a high resistance is put in the line for the light fraction the mercury stream starts to spread from the very beginning. The fractionation ratio now increases continually until, again, turbulent motion reaches the centre of the stream and the separation efficiency decreases as before.

It is therefore felt that direct observation as to how the mercury stream behaves and especially as to where the mercury condenses may give valuable information. This method was used by us as a check that a really parallel stream of flow was obtained in our experiments.

Summary.

The principle of a new diffusion chamber for diffusion in fast streaming vapours is given. The physical theory is discussed, the proper boundary conditions are determined and the corresponding solutions derived and examined. A useful approximation for rapid numerical calculations is given.

I wish to thank Professor H. C. Urey for his constant encouragement and his kind interest in this work, and Dr. F. J. Murray for his valuable aid and co-operation.

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* The efficiency of the separation should increase quasi-exponentially with the velocity of the mercury vapour, according to the equations already developed.

THE SURFACE TENSIONS OF N-CHLOROACETANILIDE-SALT-WATER MIXTURES.

By J. W. Belton.

Received 1*st December*, 1936.

The application of thermodynamic considerations to the surfaces of salt solutions shows that the salt concentration at the surface is less than that in the bulk of the solution. The writer[1] has previously attempted to find the effect of the presence of other dissolved molecular species on the surface concentration of the components adsorbed, and for the case of ternary solutions containing non-electrolyte found the effect of the addition of ethyl alcohol and of acetic acid at constant concentration on the adsorption of water at the surface of various salt solutions.

When the concentration of one component remains constant, the calculation of the surface adsorption by means of the Gibbs equation requires a knowledge of the surface concentration of the non-electrolyte and of its activity coefficient in the presence of salt. A more exact calculation of the surface adsorption may be made if the non-electrolyte is added at constant activity rather than constant concentration. It is convenient for this purpose to use a slightly soluble non-electrolyte, the solubility of which is sufficient, however, to produce a measurable change in the surface tension even in strong salt solutions, in which the salting out may be considerable. N-Chloroacetanilide appeared to be a suitable substance, and measurements of the surface tensions of ternary solutions of which it was a component were therefore made.

Experimental.

The surface tensions were measured by the modification of the bubble pressure method previously described by the writer.[1] The radius of the jet used in this investigation was 0·0104 cm. All measurements were made at 25° C. Solutions were made up by weight from salts of Analar grade, which had been treated in certain cases for the removal of water; the hydrated forms of barium chloride and magnesium sulphate were used and allowance made for the additional water thus introduced. The surface tension of the water from which the solutions were made was 72·01 dyne/cm. N-Chloroacetanilide was prepared by the chlorination of acetanilide by means of potassium hypochlorite solution according to the method recommended by Orton. The almost pure product was recrystallised from glacial acetic acid, traces of which were removed by washing with water.

An excess of N-chloroacetanilide was shaken with the salt solution in a sealed bottle, completely immersed in a thermostat at 25° C., for about five hours, this period having been found necessary for saturation from preliminary experiments. The bottle was then quickly removed from the thermostat, the seal broken, and a sample of the liquid drawn quickly through a loose plug of wool into the experimental cell at 25°. The level of the liquid was then adjusted so that its surface was coincident with the jet and the surface tension measured. Blackened vessels were not practicable, but in no case was the solution exposed to a strong light. In those experiments in which the concentration of non-electrolyte was kept constant, ternary solutions were made up by weight from salt and a stock solution of N-chloroacetanilide, the composition of which was determined by titration with thiosulphate. This stock solution was used as soon as it was prepared in order to avoid errors due to the decomposition of the solute. The solubility of N-chloroacetanilide is 0·00134 moles/litres which, if the activity coefficient is regarded as unity in a solution of this concentration, may be taken as the activity of the dissolved non-electrolyte when in equilibrium with the solid phase.

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[1] Belton, *Trans. Faraday Soc.*, 1935, **31**, 1420.

The results are given in Table I., in which *m* is the concentration of salt in moles per 1000 gm. of water, *h* is the maximum bubble pressure in centimetres of butyl phthalate, and γ is the surface tension in dyne/cm. calculated from the relation

TABLE I.

Salt.	*m.*	*h.*	γ.	$\Delta\gamma$.	*k.*
NaCl . .	0·501	12·355	65·96	0·72	1·44
	1·002	12·45	66·41	1·17	1·17
	2·004	12·745	67·99	2·75	1·38
	3·006	13·09	69·35	4·11	1·37
KCl . .	0·501	12·33	65·78	0·54	1·08
	1·002	12·42	66·24	1·00	1·00
	2·004	12·67	67·59	2·35	1·17
	3·006	12·89	68·76	3·52	1·17
	4·008	13·075	69·74	4·50	1·12
LiCl . .	0·919	12·415	66·23	0·99	1·08
	1·544	12·56	67·00	1·76	1·14
	1·851	12·60	67·21	1·97	1·06
	3·386	12·98	69·24	4·00	1·18
	3·774	13·05	69·59	4·35	1·15
$CaCl_2$ . .	0·447	12·375	66·02	0·78	1·75
	0·752	12·51	66·73	1·49	1·98
	1·062	12·635	67·40	2·16	2·03
	1·360	12·79	68·22	2·98	2·19
$BaCl_2$ . .	0·484	12·38	66·03	0·79	1·63
	0·953	12·65	67·47	2·23	2·34
	1·404	12·77	68·12	2·88	2·05
$MgSO_4$ . .	0·489	12·43	66·30	1·06	2·17
	0·997	12·68	67·63	2·39	2·40
	1·868	13·44	71·69	6·45	3·45
	2·620	14·43	76·98	11·74	4·48
Sucrose .	0·5	12·265	65·42	0·18	0·36
	1·0	12·355	65·91	0·67	0·67
	2·0	12·51	66·73	1·49	0·75
	3·0	12·66	67·52	2·28	0·76
$MgSO_4$ only .	0·997	13·89	74·09	2·08	2·09
	1·868	14·30	76·28	4·27	2·28
	2·620	14·80	78·96	6·95	2·65

$$\gamma = \frac{rg}{2}\left(h\rho - \tfrac{2}{3}r\rho_1\right),$$

where r is the radius of the jet, g is 981·2 cm./sec.^{2}, ρ is the density of butyl phthalate at 25° C. and ρ_1 is the density of the solution. The surface tension increment, $\Delta\gamma$, is the difference between the surface tension of the solution and that of a saturated N-chloroacetanilide solution containing no salt (that is a solution in which the activity of N-chloroacetanilide is the same as in the salt solutions). The final column gives the values of k calculated from the relation

$$\Delta\gamma = km$$

which is analogous to that which holds for solutions containing only salt. A similar relation holds if the increments are taken as the difference between the surface tension of the pure solvent and that of the ternary solution, but with different values of k. The results show that k is constant for solutions containing the alkali halide salts. The behaviour of salts of higher valence type, for which k increases with increasing salt concentration, might be anticipated as the salting out of non-electrolyte will increase with salt concentration, and the higher the valence type of the salt, the more effective it will be.

Application of the Gibbs Equation.

For a ternary solution the Gibbs equation takes the form

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 - \Gamma_3 d\mu_3 \quad . \quad . \quad . \quad (1)$$

where Γ_1, Γ_2, Γ_3 are the surface concentrations, and μ_1, μ_2, μ_3 are the chemical potentials of the components. N-Chloroacetanilide lowers the surface tension of water, and so will be positively adsorbed at the surface ; water is also positively adsorbed at the surface of salt solutions. The dividing surface for the ternary solution may be drawn so that the surface concentration of salt is zero. For this case

$$d\gamma = -\Gamma_2 d\mu_2 - \Gamma_3 d\mu_3 \quad . \quad . \quad . \quad . \quad (2)$$

Combination of this relation with the Duhem-Margules equation, according to which

$$n_1 d\mu_1 + n_2 d\mu_2 + n_3 d\mu_3 = 0 \quad . \quad . \quad . \quad . \quad (3)$$

where n_1, n_2, n_3 are the mole fractions of the components, gives

$$d\gamma = -\Gamma_2 d\mu_2 + \Gamma_3 \frac{n_1}{n_3} d\mu_1 + \Gamma_3 \frac{n_2}{n_3} d\mu_2 \quad . \quad . \quad (4)$$

In terms of activities this becomes

$$d\gamma = -\Gamma_2 RTd \log a_2 + \Gamma_3 \frac{n_1}{n_3} 2RTd \log a_{\pm} + \Gamma_3 \frac{n_2}{n_3} RTd \log a_2 \quad (5)$$

in which a_2 is the activity of the non-electrolyte and $a_{\pm}$ is the mean activity of the salt. If the activity of the non-electrolyte remains constant while the concentration (and the activity) of the salt varies, then

$$\left(\frac{\partial\gamma}{\partial m_1}\right)_{\mu_2} = \Gamma_3 \frac{n_1}{n_3} 2RT \left(\frac{\partial \log a_{\pm}}{\partial m_1}\right)_{\mu_2} = \Gamma_3 \frac{m_1}{55\cdot 55} 2RT \left[\frac{1}{m_1} + \left(\frac{\partial \log f_{\pm}}{\partial m_1}\right)_{\mu_2}\right] \quad (6)$$

where $f_{\pm}$ is the mean activity coefficient of the salt. The concentration of the non-electrolyte is small throughout, and its influence on the activity coefficient of the salt may be neglected. Table II. gives the values of Γ_3 in moles/sq. cm. × 10^{10} calculated from this equation. The activity coefficients of alkali chloride solutions were obtained from the data of Pease and Nelson ;[2] these values were obtained from vapour pressure measurements, and it is stated that they are in good agreement with those found by E.M.F. methods. The activity coefficients of calcium chloride and barium chloride were taken from the paper of Scatchard and Tefft,[3] and those of magnesium sulphate from that of Robinson and Jones.[4] Values of $\Delta \log f_{\pm}/\Delta m_1$ were calculated for small concentration intervals, and $\Delta \gamma/\Delta m_1$ found for the same interval. For the alkali chloride solutions $\partial \gamma/\partial m_1$ is given by the mean value of k, but for the other solutions it was obtained graphically. The values of Γ given in the table are for a number of rounded concentrations, but no attempt has been made to smooth them.

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[2] Pease and Nelson, *J. Amer. Chem. Soc.*, 1932, 54, 3544.

TABLE II.

	m_1.	0·3.	0·5.	0·7.	1·0.	1·25.	1·75.	2·25.	2·75.	3·25.
NaCl	${}_0\Gamma_3$	23·0	20·8	20·3	19·5	18·8	17·4	13·7	12·8	12·0
	Γ_3	18·4	16·6	16·2	15·5	15·0	14·0	10·4	10·2	9·8
KCl	${}_0\Gamma_3$	21·2	21·0	21·1	20·5	20·3	19·9	19·6	17·4	17·4
	Γ_3	14·1	14·0	14·0	13·8	13·5	13·4	13·2	12·4	12·4
LiCl .	${}_0\Gamma_3$	19·2	18·2	17·0	14·8	12·0	10·3	9·3	8·5	8·0
	Γ_3	13·4	12·5	11·2	10·0	8·1	7·0	6·3	5·9	5·5

	m_1.	0·15.	0·25.	0·4.	0·7.	0·9.	1·25.	1·75.	2·25.	
$CaCl_2$	${}_0\Gamma_3$	37·7	33·8	29·5	24·0	21·3	19·0	—	—	
	Γ_3	21·2	19·2	19·9	17·9	15·8	15·1	—	—	
$BaCl_2$	${}_0\Gamma_3$	40·0	38·1	35·9	32·2	30·4	28·6	—	—	
	Γ_3	21·9	21·0	19·9	18·9	18·3	17·3	—	—	
$MgSO_4$	${}_0\Gamma_3$	44·5	46·0	46·4	45·9	45·0	39·5	35·1	32·5	
	Γ_3	46·7	48·3	47·6	45·3	43·8	72·1	67·3	63·1	

The table also gives the surface adsorption of water for solutions containing only salt; these have been calculated from the Gibbs equation applied to a binary system:

$$\frac{d\gamma}{dm} = {}_0\Gamma_3 2RT \frac{m}{55 \cdot 55}\left\{\frac{1}{m} + \frac{d \log f_{\pm}}{dm}\right\} \quad . \quad . \quad . \quad (7)$$

The surface tension data used were those previously published by the writer, except in the case of magnesium sulphate, which were measured for the present purpose and are recorded at the end of Table I.

The effect of N-chloroacetanilide is to reduce the surface adsorption of water in all cases except that of magnesium sulphate. Its influence is best shown by the plot of Γ_3 and of ${}_0\Gamma_3$ against salt concentration. For the alkali chlorides the two curves are almost parallel, but at higher salt concentrations the lower curve of the ternary system is a little less steep than that for the binary system. There seems to be a kink in each curve at 1·4 molal for lithium chloride and at about 2·4 molal for sodium and potassium chlorides. For potassium chloride there is little change in the water adsorption over the whole range of salt concentration, although the concentration of the non-electrolyte varies considerably. The adsorption curves for calcium and barium chlorides are rather different. The adsorption for binary solutions falls with salt concentration, so that the two curves converge rapidly. For magnesium sulphate the surface adsorption is greater for the ternary solution, and increases very rapidly with salt concentrations greater than 1·0 *M*. This result is connected with the large values of $(\partial\gamma/\partial m)\mu_2$ which are greater than for the binary system, and probably with the extensive salting out in the strong solutions. The extent of salting out is shown in Table III., which gives the value of $(\partial \log f_2/\partial m_1)\mu_2$ for typical salts.

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[3] Scatchard and Tefft, *J. Amer. Chem. Soc.*, 1930, **52**, 2272.

[4] Robinson and Jones, *ibid.*, 1936, **58**, 959.

The thickness of the adsorbed layer in Å may be obtained by multiplying the tabulated values of Γ_3 by the molecular weight of water. The area occupied per molecule in the layer is given by $1/\Gamma_3 N$. If the the area of cross-section of a water molecule is assumed to be of the order 7 Å², the adsorption which corresponds to a saturated unimolecular layer is 23×10^{-10} moles/sq. cm. In some cases the value of Γ_3 found is greater than this value. The factor by which the thickness of the adsorbed layer is reduced by the addition of N-chloroacetanilide to solutions of various salts at different concentrations is given in Table IV.

TABLE III

	m_1	$(\partial \log f_2 \partial m_1)\mu_2$
NaCl	0·5 — 3·9	0·35
BaCl$_2$	0·2 — 1·3	0·50
MgSO$_4$	0·2 — 1·0	1·05

TABLE IV

m.	NaCl.	KCl.	LiCl.	CaCl$_2$.	BaCl$_2$.	MgSO$_4$.	Sucrose.
0·3	0·80	0·67	0·69	0·59	0·56	1·04	0·54
0·7	0·80	0·67	0·66	0·75	0·59	0·99	0·70
1·25	0·80	0·67	0·68	0·80	0·61	1·8	—
2·25	0·80	0·68	0·68	—	—	1·9	0·80
3·25	0·86	0·71	0·69	—	—	—	—

Solutions containing N-Chloroacetanilide and Sucrose.

The surface tensions of sucrose solutions are greater than that of water; it may be assumed, then, that water is positively adsorbed at the surface of solutions containing N-chloroacetanilide and sucrose. The dividing surface may be drawn so that the concentration of sucrose is zero, and the Gibbs equation may be written

$$d\gamma = -\Gamma_2 d\mu_2 - \Gamma_3 d\mu_3$$

where the subscripts have the same significance as before. For constant N-chloroacetanilide activity we have

$$\left(\frac{\partial\gamma}{\partial m_1}\right)_{\mu_2} = -\Gamma_3\left(\frac{\partial\mu_3}{\partial m_1}\right)_{\mu_2} \qquad . \quad . \quad . \quad (8)$$

If p_3 is the vapour pressure of water above the solution, then

$$\left(\frac{\partial \gamma}{\partial m_1}\right)_{\mu_2} = -\Gamma_3 RT\left(\frac{\partial \log p_3}{\partial m_1}\right)_{\mu_2}$$

or

$$\Gamma_3 = -\left(\frac{\partial \gamma}{\partial m_1}\right)_{\mu_2} \Big/ RT\left(\frac{\partial \log p_3}{\partial m_1}\right)_{\mu_2} \quad . \quad . \quad . \quad (9)$$

The amount of N-chloroacetanilide present is small, and its effect on the vapour pressure of water may be neglected; $(\partial \log p_3/\partial m_1)_{\mu_2}$ may thus be obtained from the vapour pressures of sucrose solutions. Values of Γ_3 in moles/sq. cm. $\times 10^{10}$ calculated in this way from the surface tension data recorded in Table I. are given in Table V.

TABLE V

m.	${}_0\Gamma_3$.	Γ_3.
0·25	29	15
0·7	20	14
1·5	17	14
2·5	15	12

Sodium Chloride Solutions containing N-Chloroacetanilide at Constant Concentration.

A number of measurements were made in which the concentration of N-chloroacetanilide was kept constant (= 0·00795 moles/litres). This concentration had to be high enough to produce a measurable effect on the surface tension, and low enough to be soluble in the strongest salt solution. The results are given in Table VI. The surface tensions appear to reach a limiting value as the salt concentration increases (compare the values of $\partial\gamma/\partial m_1$).

The application of the Gibbs equation is not so simple as in the other ternary solutions investigated. From (5)

$$\left(\frac{\partial \gamma}{\partial m_1}\right)_{m_2} = -\Gamma_2 RT\left(\frac{\partial \log f_2 m_2}{\partial m_1}\right)_{m_2} + \Gamma_3\frac{n_1}{n_3}2RT\left(\frac{\partial \log f_\pm m_1}{\partial m_1}\right)_{m_2}$$
$$+ \Gamma_3\frac{n_2}{n_3}RT\left(\frac{\partial \log f_2 m_2}{\partial m_1}\right)_{m_2} \quad (10)$$

where f_2 is the activity coefficient of the non-electrolyte. This may be written

$$\left(\frac{\partial \gamma}{\partial m_1}\right)_{m_2} = -\Gamma_2 RT\left(\frac{\partial \log f_2}{\partial m_1}\right)_{m_2} + \Gamma_3\frac{n_1}{n_3}2RT\left[\frac{1}{m_1} + \left(\frac{\partial \log f_\pm}{\partial m_1}\right)_{m_2}\right]$$
$$+ \Gamma_3\frac{n_2}{n_3}RT\left(\frac{\partial \log f_2}{\partial m_1}\right)_{m_2} \quad (11)$$

from which

$$\Gamma_3 = \frac{n_3\left[\frac{1}{RT}\left(\frac{\partial \gamma}{\partial m_1}\right)_{m_2} + \Gamma_2\left(\frac{\partial \log f_2}{\partial m_1}\right)_{m_2}\right]}{2n_1\left[\frac{1}{m_1} + \left(\frac{\partial \log f_2}{\partial m_1}\right)_{m_2}\right] + n_2\left(\frac{\partial \log f_2}{\partial m_1}\right)_{m_2}} \quad . \quad (12)$$

Adsorptions in moles/sq. cm. $\times 10^{10}$ calculated from this equation are given in Table VI. The value of $\partial \log f_2/\partial m_1$ was obtained from solubility measurements; it appears to be constant at salt concentrations greater than 0·5 *M*, but decreases at lower values. Γ_2 was taken as $1{\cdot}60 \times 10^{-10}$ moles/sq. cm. (*cf.* Table VII.).

TABLE VI.

Surface Tensions of Aqueous N-Chloroacetanilide Solutions.

m.	h.	γ.
—	—	72·01
0·00795	13·15	70·14
0·0134	12·23	65·24

Surface Tensions of N-Chloroacetanilide-Salt-Water Mixtures.

m.	h.	γ	$\Delta\gamma/\Delta m_1$.	$\partial \log f_2/\partial m_1$.	${}_0\Gamma_3$.	Γ_3
0·5	13·225	70·56	0·70	0·35	20·0	23·4
1·0	13·27	70·78	0·31	0·37	19·3	20·0
2·0	13·285	70·87	0·0	0·37	15·0	—
3·0	13·28	70·84	0·0	0·37	12·0	—

The Adsorption of N-Chloroacetanilide and the Structure of the Surface Layer.

The adsorption of N-chloroacetanilide in the absence of salt may be calculated from the data given in the first part of Table VI. At these dilutions its activity may be taken as equal to its concentration, and the adsorption obtained from

$$\Gamma = \frac{1}{RT} \cdot \frac{\Delta\gamma}{\Delta \log m_2}.$$

The value for $m_2 = 0{\cdot}008$ found in this way is $1{\cdot}4 \times 10^{-10}$ moles/sq. cm., which corresponds to an area of 120 Å^2 per molecule in the surface. The layer is thus not nearly saturated.

The variation of the surface tension of ternary solutions with salt concentration at constant concentration of N-chloroacetanilide (equation (10)) provides a method for the calculation of the adsorption of the latter at the surface of saturated solutions. When the salt concentration is such that the solution is saturated with respect to the non-electrolyte equations (6) and (11) will be simultaneously applicable, and we obtain

$$\Gamma_2 = \frac{\Gamma_3 2n_1\left[\frac{1}{m_1} + \left(\frac{\partial \log f_\pm}{\partial m_1}\right)_{m_2}\right] + \Gamma_3 n_2\left(\frac{\partial \log f_2}{\partial m_1}\right)_{m_2} - \frac{n_3}{RT}\left(\frac{\partial \gamma}{\partial m_1}\right)_{m_2}}{n_3\left(\frac{\partial \log f_2}{\partial m_1}\right)_{m_2}} \qquad (13)$$

As the solution approaches saturation with respect to the non-electrolyte $(\partial\gamma/\partial m_1)_{m_2}$ falls until at the saturation point it becomes zero (*cf.* Table VI.), and (13) then becomes

$$\Gamma_2 = \Gamma_3 \frac{2n_1\left[\frac{1}{m_1} + \left(\frac{\partial \log f_\pm}{\partial m_1}\right)_{m_2}\right]}{n_3\left(\frac{\partial \log f_2}{\partial m_1}\right)} + \Gamma_3 \frac{n_2}{n_3} \quad . \quad . \quad (14)$$

The values of Γ_2 in moles/sq. cm. × 10^{10} calculated from this equation are given in Table VII. for three typical salts; values of Γ_3 from Table II. were used, and values of $(\partial \log f_2/\partial m_1)m_2$ were taken from previously published data of the writer.[5] Strictly these latter refer to constant activity of the non-electrolyte, but the error so introduced will be small.

TABLE VII.

NaCl.							
m_1	0·3	0·5	0·7	1·0	1·25	2·25	3·25
Γ_2	1·60	1·60	1·60	1·58	1·60	1·59	1·60
x	0·78	0·70	0·69	0·66	0·64	0·46	0·42
A_2	23	31	32	35	37	55	59
BaCl$_2$.							
m_1	0·15	0·25	0·4	0·7	0·9	1·125	
Γ_2	1·29	1·29	1·33	1·38	1·41	1·41	
x	0·93	0·89	0·86	0·81	0·78	0·73	
A	9	14	16	23	26	31	
MgSO$_4$.							
m_1	0·15	0·25	0·4	0·7	1·25	1·75	2·25
Γ_2	0·78	0·79	0·79	0·78	1·16	2·01	2·57

For solutions in which the concentration of the non-electrolyte is low, n_2/n_3 may be neglected and if the value of Γ_3 given by (6) is substituted in (14) we obtain

$$\Gamma_2 = \frac{1}{RT}\left(\frac{\partial\gamma}{\partial m_1}\right)_{\mu_2} \bigg/ \left(\frac{\partial \log f_2}{\partial m_1}\right)_{\mu_2} = \frac{1}{RT}\left(\frac{\partial\gamma}{\partial \log f_2}\right)_{\mu_2}. \qquad (15)$$

If the salting-out coefficient is constant, as is the case for N-chloroacetanilide, then Γ_2 will vary with the salt concentration in the same way as does the surface tension of the saturated non-electrolyte solution, and for the alkali chlorides will be constant.

It is found that while for sodium chloride Γ_2 is constant over a wide concentration range at a value slightly higher than that in the absence of salt, for barium chloride and magnesium sulphate Γ_2 increases with increasing salt concentration. The table also gives the fraction (x) of the surface occupied by water molecules, assuming their area (A_1) to be 7 Å^2, the value obtained from the molecular volume; x is given by $A_1\Gamma_3 N \times 10^{-16}$, and the area ($A_2$) in Å^2 available per molecule of non-electrolyte is given by $(10^{16} - A_1\Gamma_3 N)/\Gamma_2 N$. For sodium chloride solutions this available area, which increases with increasing salt concentration, is sufficient to accommodate an N-chloroacetanilide molecule, of area of about 30 Å^2. The area available at the surface of the barium chloride solutions is, however, less than this, and in order that the layer should be unimolecular the N-chloroacetanilide must be orientated differently (possibly vertically) at the surface, or the area of the water molecule must be less than 7 Å^2. The water adsorbed at the surface of the magnesium sulphate solutions corresponds to more than a complete unimolecular layer of molecules of area 7 Å^2. In order to leave sufficient space for molecules of N-chloroacetanilide of 30 Å^2, the area per molecule of water is reduced to 2 Å^2, which is a possible figure if they were arranged vertically in the surface.

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[5] Belton, *Proc. Leeds Phil. Soc.*, 1931, **2**, 178.

Summary.

The effect of the presence of N-chloroacetanilide on the surface tensione of various salt solutions has been examined. In all cases the surfacs tension was lowered, and in the case of the alkali chlorides a linear relation between the surface tension increment and the salt concentration was found. In order to avoid difficulties in the calculation of the amount of water adsorbed by means of the Gibbs equation, measurements were made in solutions containing the non-electrolyte at constant activity. For the alkali chloride solutions the adsorption-salt concentration curve is nearly parallel to that for solutions containing salt alone; for the alkaline earth chlorides the water adsorption falls, while that for the salt alone falls more rapidly with increasing salt concentration. The adsorption of water at the surface of a solution containing N-chloroacetanilide at constant concentration has also been calculated; the adsorption of water on the ternary solution is found to fall more rapidly with increasing salt concentration than for the binary. It is also shown that the presence of sucrose produces a reduction in the water adsorption. The adsorption of N-chloroacetanilide at the surface of the ternary solutions has been calculated and the structure of the surface layer discussed.

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ON THE INTRODUCTION OF THERMODYNAMIC VARIABLES INTO REACTION KINETICS.

By M. G. Evans and M. Polanyi.

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The semi-thermodynamical treatment of reaction kinetics suggested by the present authors[1] and Wynne-Jones and Eyring[2] has received comments which call for elucidation of various points.

(1) Firstly, we wish to elucidate the relationship between the Arrhenius' concept of active molecules and the concept of the transition state. According to Arrhenius, a reaction A → B has to be written $A \rightarrow A^* \rightarrow B$, the reaction velocity constant is determined by the product of the equilibrium constant K^* between the substance in its normal state A and in its activated state A*, and the reaction velocity constant k^* if the reaction $A^* \rightarrow B$

$$k = K^*k^*.$$

This leads to

$$\frac{\partial \ln k}{\partial T} = \frac{\partial \ln K^*}{\partial T} + \frac{\partial \ln k^*}{\partial T} \quad . \quad . \quad . \quad (1)$$

which is identical with Arrhenius' equation

$$\frac{\partial \ln k}{\partial T} = \frac{Q}{RT^2}$$

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[1] (*a*) *Trans. Faraday Soc.*, 1935, 31, 875; (*b*) 1936, 32, 1333.
[2] *J. Chem. Physics*, 1935, 3, 492.

if k^* is independent of the temperature and Q is the heat of reaction $A \rightarrow A^*$.

The theory offers no explanation for the assumptions that the reaction $A^* \rightarrow B$ is rate determining and that $\frac{\partial \ln k^*}{\partial T} \sim 0$. It is also immediately obvious that no conclusion can be drawn as to the influence of hydrostatic pressure on reaction velocity since all we obtain is

$$\frac{\partial \ln k}{\partial \pi} = \frac{\partial \ln K^*}{\partial \pi} + \frac{\partial \ln k^*}{\partial \pi} \quad . \quad . \quad . \quad . \quad (2)$$

and nothing is known of the dependence of lu k^* on pressure. The procedure merely amounts to shifting the problem of the influence of hydrostatic pressure on the reaction velocity constant from k to k^*.

Considerations of the transition state lead to results which cannot be derived from the idea of the Arrhenius complex since it is a totally different conception. Whereas A represents a molecular species and as such extends over a finite range in the direction of all its co-ordinates, the extension of the transition state is infinitesimal in the direction of the reaction co-ordinate. Hence, whereas the concentration of the Arrhenius complex A^* at equilibrium is a finite quantity which is K^*c_A that of the transition state is an infinitesimal magnitude $\mathbf{K} \, . \, dl \, . \, c_A$.

To avoid confusion we suggest that the term equilibrium constant for **K** as used in our previous papers should be abandoned since considering its dimension it is not in the nature of an equilibrium constant; the term *equilibrium factor* might be suitable. The equilibrium constant between the initial and transition states is in fact $\mathbf{K}dl$ and it is primarily this magnitude which should be treated thermodynamically.

(2) Wynne-Jones and Eyring[2] consider that there is a choice as between **K** and another equilibrium factor K^+

$$\mathbf{K} = K^+ \frac{(2\pi m^+ kT)^{\frac{1}{2}}}{h}$$

which might be settled by convention. We suggest that only **K** can be regarded as a thermodynamic variable since $\frac{\partial}{\partial \chi}(RT \ln \mathbf{K}) = -\frac{\partial F}{\partial \chi}$ (where F is the free energy change between the initial and transition states) and thus is defined by the derivative of the free energy of the transition state with respect to χ, whereas the same does not hold for K^+. For example $\frac{\partial \ln \mathbf{K}}{\partial T} = \frac{Q}{RT^2}$ where Q is the formation heat of the transition state, whereas from $\frac{\partial \ln K^+}{\partial T} = \frac{Q'}{RT^2}$ a heat Q' arises for which we can see no physical meaning.

(3) In one of our papers mentioned above[1] we have derived the influence of pressure on the reaction constant from the transition state method in the following way:

$$k = \mathbf{K}v/2$$

$$\frac{\partial \ln k}{\partial \pi} = \frac{\partial \ln \mathbf{K}}{\partial \pi} + \frac{\partial \ln v/2}{\partial \pi} \quad . \quad . \quad . \quad (3)$$

since $\frac{\partial \ln v/2}{\partial \pi}$ is negligible

$$\frac{\partial \ln k}{\partial \pi} = \frac{\partial \ln \mathbf{K}}{\partial \pi} = \frac{V_1 - V_\tau}{RT} \quad . \quad . \quad . \quad (4)$$

and we obtain for the molar volume of the transition state V_τ

$$V_\tau = -RT\frac{\partial \ln k}{\partial \pi} + V_1.$$

We have then proceeded to discuss the probable volume change between the initial and transition states and compared the theoretical estimate with values which we calculate from observations of Gibson, Fawcett, and Perrin.[3]

In a recent paper Moelwyn-Hughes [4] has stated that the same equation has been suggested by van't Hoff on the following lines :

$$\text{From } K = \frac{k_2}{k_1} \quad \text{and} \quad \frac{\partial \ln K}{\partial \pi} = -\frac{(V_2 - V_1)}{RT} \quad . \quad . \quad . \tag{4a}$$

$$\left(\frac{\partial \ln k_2}{\partial \pi}\right) - \left(\frac{\partial \ln k_1}{\partial \pi}\right) = -\frac{(V^* - V_1)}{RT} + \frac{(V^* - V_2)}{RT} \quad . \tag{5}$$

where V^* is an arbitrary volume. In a further step the assumption is made that

$$\frac{\partial \ln k_2}{\partial \pi} = -\frac{(V^* - V_1)}{RT} \quad . \quad . \quad . \quad . \quad . \tag{6}$$

$$\frac{\partial \ln k_1}{\partial \pi} = -\frac{(V^* - V_2)}{RT} \quad . \quad . \quad . \quad . \quad . \tag{7}$$

where now V^* has an unique value which is the volume of the active molecules in the Arrhenius sense.

In actual fact van't Hoff [5] has not suggested equations (5), (6) and (7) but pointed out that the equation equivalent to (4*a*)

$$\frac{\partial \ln k_2}{\partial \pi} - \frac{\partial \ln k_1}{\partial \pi} = \frac{\Delta v}{RT} = \frac{V_2}{RT} - \frac{V_1}{RT}$$

(in which k_2 and k_1 are velocity constants Δv is the volume change caused by the reaction, V_2 and V_1 are the initial and final volumes) may be divided up into two possible equations of the form

$$\frac{\partial \ln k}{\partial \pi} = \frac{V}{RT} + A \quad . \quad . \quad . \quad . \quad . \tag{8}$$

where A is an undefined magnitude which is independent of pressure. The omission of the subscripts shows that the dividing up has been carried out in two halves with equal subscripts so that $V = V_1$ for $k = k_1$ and $V = V_2$ for $k = k_2$. For volume differences such as appear in Moelwyn-Hughes' equation, van't Hoff uses not V but Δv. But even if in spite of all this we were to identify V with a magnitude $V - V^*$ the fact would remain that equation (8) contains the undefined magnitude A which would have to be omitted to obtain an equation of the form quoted by Moelwyn-Hughes. Such omissions are not permissible. In the present case the mistake is particularly serious as the significance of the equation is completely changed by it. In fact, so long as the quantity A is present it is impossible to determine V from $\frac{\partial \ln k}{\partial \pi}$ and thus all the calculations carried out by Moelwyn-Hughes are based on the omission of the quantity A. We note further that the volume of the active molecules in the Arrhenius sense which, according to Moelwyn-Hughes, van't Hoff has deduced, is not mentioned by van't Hoff at all. In fact, where, on page 230,[5] van't Hoff makes reference to Arrhenius' theory he shows no evidence that he accepts this theory but raises difficulties connected with it and suggests that his own equation does not give rise to these difficulties.* There is, therefore, no evidence whatsoever that van't Hoff drew any conclusions with regard to the volume of active molecules in the Arrhenius sense.

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[3] *Proc. Roy. Soc., A.*, 1935, 150, 223.

[4] *Trans. Faraday Soc.*, 1936, 32, 1723.

[5] *Vorl. über Theor. u. Physikalische Chemie*, I., 236, *Braunschweig*, 1901.

The reader may find it difficult to accept this statement in view of the remarks made by Moelwyn-Hughes on page 1737 of his paper. Reference is there made to " van't Hoff's view " that $\Delta V^* = (V_1 - V^*)$ is zero for optical isomerisations. A reference to the top of the same page shows, however, that van't Hoff's assumption (as quoted correctly there) applies to $\Delta V = V_\beta - V_\alpha$ where V_α and V_β are the volumes of the initial and the *final* states respectively, and not to ΔV^*. (We might mention that we see no reason why $\Delta V = 0$ should necessitate or even make it likely that ΔV^* should also be zero.)

Finally, we take this occasion to note that formula (8) suggested by van't Hoff as a possible equation has the same general form $\frac{\partial \ln k}{\partial \pi} = const.$ as our own equation.

(4) In the light of our present knowledge of reaction mechanism the active molecules in the Arrhenius sense have become meaningless. The only way of reintroducing the concept of these active molecules would be by identifying them with the transition state which, as we explained in paragraph (1) is incorrect and gravely misleading.

We see no reason why equation

$$\frac{\partial \ln k}{\partial \pi} = \frac{V_1 - V_\tau}{RT}$$

which, we believe, has been satisfactorily derived from theoretical considerations † should now be substituted by an equation of identical form introduced as an arbitrary hypothesis to which an interpretation is attached based on concepts which are incorrect.

(5) There is yet another section of the paper by Moelwyn-Hughes which we wish to discuss because the results clash with some of our own deductions.

An examination of the influence of hydrostatic pressure on the activation energy E_A shows [1b] (by combination of equations 20 on page 1340),

$$E_A = E_0 + \pi(V_1 - V_\tau)\left\{1 - T\left(\frac{\partial \ln(V_1 - V_\tau)}{\partial T}\right)_\pi\right\} \quad . \quad (9)$$

where E_0 is the value of E_A for $\pi = 0$.

On the other hand Moelwyn-Hughes gives the expression

$$E_A = \Delta E^* + \pi \Delta V^*\left\{1 - T\left(\frac{\partial \ln \Delta V^*}{\partial T}\right)_\pi\right\} - \Delta V^*\left(\frac{\partial \pi}{\partial T}\right)_v \quad . \quad (10)$$

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* On page 230 van't Hoff discusses the possibilities of dividing up the reaction isochor $\frac{\partial \ln k_2/k_4}{\partial T} = \frac{Q}{RT^2}$ and mentions various solutions including Arrhenius' equation and a different equation suggested by himself.

† We do not know whether this view is shared by Moelwyn-Hughes since he does not refer to our work on the pressure coefficient of reaction velocity.

This can be brought to the same form as (9) by identification of $(V_1 - V_\tau)$ with ΔV^* and by setting

$$\Delta E^* - \Delta V^* \left(\frac{\partial \pi}{\partial T}\right)_v = E_0. \quad . \quad . \quad . \quad (11)$$

The magnitude ΔE^* is defined by Moelwyn-Hughes as follows: he assumes that the velocity constant k is of the form

$$k = const.\ e^{-\Delta F^*/RT} \quad . \quad . \quad . \quad . \quad (12a)$$

where ΔF^* is a critical free energy of the reacting molecules. Equation (12*a*) is then rewritten according to thermodynamics

$$k = const.\ e^{-\Delta E^*/RT} e^{-\pi \Delta V^*/RT} e^{T\Delta S^*/RT} \quad . \quad . \quad (12)$$

From these two equations we conclude that $E_0 \equiv \Delta E^*$ and that equation (11) is, therefore, incorrect. By definition

$$E_0 \equiv \left(\frac{\partial \ln k}{\partial T}\right)_{\pi = 0} RT^2 \quad . \quad . \quad . \quad (13)$$

From equation (12) we obtain by differentiating logarithmically with respect to temperature at $\pi = 0$ that

$$\left(\frac{\partial \ln k}{\partial T}\right) = -\frac{\partial(\Delta F^*/RT)}{\partial T} = \Delta E^*$$

which in combination with (13) gives $\Delta E^* \equiv E_0$. It follows that equation (11) is in contradiction to thermodynamics.

This erroneous equation is arrived at in the following way: Firstly, the equation (12) is identified (through an intermediate identity) with the semi-empirical equation $k_2 = pZ_2e^{-E_A/RT}$ where p and Z_2 are constants. (This first step seems unnecessary for the subsequent argument, but we quote it for the sake of accuracy.) Next the two equations are differentiated logarithmically with respect to temperature and the results set equal, the erroneous result (equation (10)) being due to a mistake in differentiation. The differentiation of both these equations must be carried out either at constant pressure or at constant volume since otherwise the temperature coefficient $\frac{\partial \ln k}{\partial T}$ has no meaning. To obtain E_A we have to differentiate at constant pressure since the measured values of E_A at ordinary pressures as well as under hydrostatic pressures are all referred to constant pressure. In carrying this out the redundant term $-\Delta V^* \left(\frac{\partial \pi}{\varrho T}\right)_v$ does not arise and we obtain our equation (9).

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THE ABSORPTION SPECTRUM OF CHLORINE TRIOXIDE AND CHLORINE HEXOXIDE.

By C. F. Goodeve and F. D. Richardson.

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Chlorine hexoxide was first obtained by Millon[1] in 1843, but his work escaped notice. Bowen[2] again prepared the substance eighty years later. Bodenstein, Harteck and Padelt[3] found that the molecule contained three atoms of oxygen to one of chlorine, and that its molecular weight, when dissolved in carbon tetrachloride, was 153-156. It was called " chlorine hexoxide " (M.W. 167). Recently it has been shown[4] that in the gaseous state, the oxide exists almost entirely, if not completely, as ClO_3—" chlorine trioxide." Magnetic measurements[5] have revealed that in the solid and liquid phases an equilibrium exists between the two forms ClO_3 and Cl_2O_6. The amount of ClO_3 present in the mixture increases with temperature, but it represents only about 1 per cent. by weight at + 10° C.

Experimental.

Preparation.

The chlorine hexoxide was prepared as for previous experiments[4] by mixing, at 0° C., a stream of oxygen, containing chlorine dioxide, with a stream of ozonised oxygen. The hexoxide formed was purified by fractional distillation, its final purity being shown by its melting-point of 3·5° C.

Absorption Spectrum of Chlorine Trioxide.

The apparatus consisted essentially of a 54 cm. long quartz absorption cell connected at one end to a reservoir of chlorine hexoxide and a quartz spiral Bodenstein pressure gauge. The other end of the cell was connected through a narrow constriction to a waste trap. The ClO_3 was caused to stream through the cell by adjusting the temperature of the reservoir, according to the pressure required in the apparatus, and by cooling the waste trap in liquid air. The products of decomposition were thus continuously removed, but the band absorption due to ClO_2—one of the products of decomposition—was not completely eliminated. Since it appeared nearer the visible than the absorption of the trioxide it could, however, be reduced so as to have little or no effect on the measurements. This band absorption produced a limitation on the absorption cell length and low values of the extinction coefficient could not be measured.

A dual path optical system was employed, with one beam passing through the absorbing medium and the other through a blank cell and an adjustable rotating sector. The light source was a hydrogen discharge tube and photographs were taken on a Hilger small quartz-spectrograph E 37. Wellington Ortho plates were used for measurements in the region up to 2200 Å. and Schumann plates for work at shorter wave-lengths.

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[1] N. A. E. Millon, *Lieb. Ann.*, 1843, **46**, 311.

[2] E. J. Bowen, *J.C.S.*, 1923, **123**, 2328; H. Booth and E. J. Bowen, *ibid.*, 1925, **127**, 510.

[3] M. Bodenstein, P. Harteck and E. Padelt, *Z. anorg. Chem.*, 1925, **147**, 233

[4] C. F. Goodeve and F. D. Richardson, *J.C.S.*, 1937. (In press.)

[5] J. Farquharson, C. F. Goodeve and F. D. Richardson, *Trans. Faraday Soc.*, 1936, **32**, 790.

From the match points on the absorption photographs decadic molar extinction coefficients were calculated, by application of the equation, $\log_{10}\frac{I_0}{I_t} = \epsilon c l$, where ϵ is the extinction coefficient, l the length in centimetres, and c the concentration in gram. mols. ClO_3 per litre.

Results.

Two plates were taken with a reservoir temperature of 0° C. and two with 3·5° C. These temperatures produced pressures of 0·31 and 0·43 mm. respectively. The logarithms of the extinction coefficients are plotted against the frequency in $cm.^{-1}$, in Fig. 1. It is seen that the absorption is continuous and that there are two maxima—one at 2780 Å. and the other extending from 2170 Å. onwards. This second maximum is apparently broad—as indicated by the dotted line.

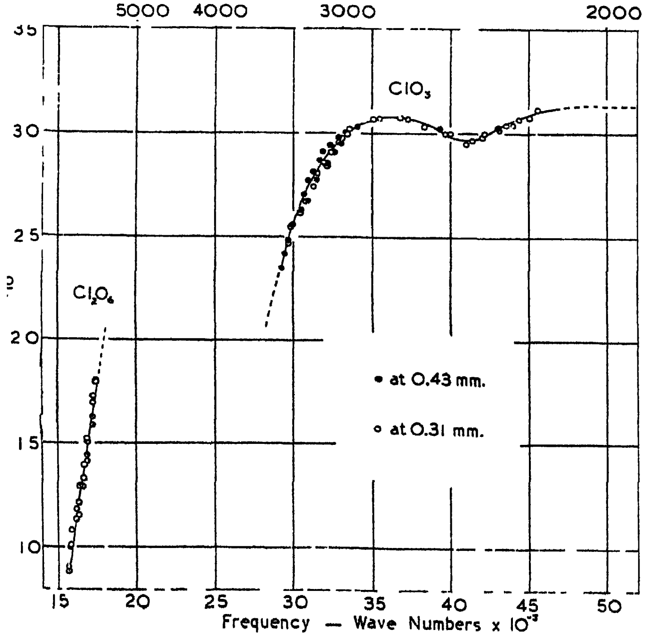


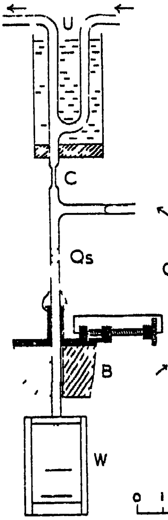
Fig. 1.

Absorption Spectrum of Chlorine Hexoxide.

On account of the strong absorption exhibited by chlorine hexoxide, it was necessary to use a very thin layer of absorbing liquid. This was achieved by using the wedge-shaped absorption cell W, made by Messrs. Adam Hilger, Ltd., as shown in Fig. 2. The dimensions of the cell were obtained by direct measurement and the angle was found to correspond to an increase of thickness of 0·00953 mm. per millimetre length. The uniformity of the cell was confirmed by a study of interference fringes. Two horizontal reference lines, parallel to the bottom of the wedge, were etched on the face of the cell.

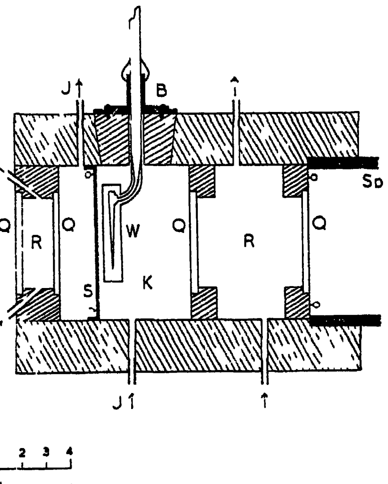
Sufficient hexoxide was distilled into the U-tube U (Fig. 2*a*) which was maintained at about − 30° C. with cooled alcohol as shown. The cooling liquid was then removed and the oxide allowed to melt and run down into the quartz cell, which was attached to the glass part of the apparatus by means of the quartz-to-soda graded seal Q*s*. The cell was cooled to − 78° C. and sealed off at the constriction C. The attached septum was used for emptying the cell after the experiment.

During the taking of photographs of the liquid hexoxide it was necessary to cool the sample to a temperature just above its melting-point, in order to avoid the rapid thermal decomposition occurring at room temperature. For this purpose the apparatus shown in Fig. 2*b* was employed. The end Sp of a Hilger E3 quartz-spectograph fitted into a teak block, with its centre hollowed out as shown. The inside was divided into three compartments by the four quartz windows Q. The temperature of the centre compartment K, which contained the cell W, was maintained at about 3°-4° C. by circulating cold dry air, as shown by the arrows at J, J. The air was dried with sulphuric acid and phosphorus pentoxide, and cooled by passing through a copper spiral immersed in liquid air. In a similar manner dry air at room temperature was circulated through the two outer compartments R, in order to prevent deposition of moisture from the atmosphere on the cold inner quartz windows. The wedge cell was supported in K by means of the teak stopper B, in which it was firmly fixed with picene wax. By means of a screw adjustment, it was possible to traverse the cell horizontally in order to use a fresh part of the absorbing layer for successive exposures, or to remove it completely from the path of the light for the purpose of blanks. A vertical slit S was situated just in front of the cell, and the spectrograph was focussed midway between the slit and the cell face. The length of the slit was adjusted so that the two reference lines and the bottom of the wedge appeared in the spectrum. A continuous range of thicknesses from 0 to 0·15 mm. was thus obtained on one spectrum photograph. The light source consisted of a hydrogen discharge tube, reinforced in the visible and red end of the spectrum by an electric light bulb. Eastman Kodak L plates, sensitive up to 9000 Å., were used. Spectrum photographs were taken through the hexoxide, and followed on the same plate by a number of blanks with different times of exposure.



a

FIG. 2*a*.



b

FIG 2*b*.

In order to determine the extinction coefficients, microphotometer tracings were made for the exposures with the chlorine hexoxide absorbing and compared with those for the blanks.

Results.

The results are plotted in Fig. 1. Evidence was found for the existence of only one absorption band extending from about 6000 Å. throughout the whole of the spectrum into the far U.V. Over the range of extinction coefficients measured there was no evidence of absorption at longer wavelengths.

Discussion.

The absorption spectrum measured here in the vapour phase has been attributed to ClO_3 and not to Cl_2O_6 or to any impurity arising from its decomposition. Evidence from the decomposition of the vapour[4] indicates that the hexoxide cannot be present at concentrations greater than 2 per cent. by volume. The values of the extinction coefficient at the two maxima are of the same order as the maxima for most gaseous compounds. Were the absorption due to Cl_2O_6, its molar extinction coefficient would reach the inordinate value of $0{\cdot}7 \times 10^5$. In another paper[4] experiments are described in which the absorption attributed to ClO_3 *decreased* in intensity at a rate parallel to the decomposition of the trioxide followed manometrically. This eliminates the possibility of the absorption being due to products of decomposition. The above assignment is also supported by the consistency of the results at the two different pressures.

The absorption in the liquid phase cannot be due to the trioxide as its concentration is too low. The magnetic measurements referred to above showed that there is only about 1 per cent. by weight of the trioxide present at the melting-point. Were the absorption here due to ClO_3 the maximum extinction measured (63 at 5700 Å.) would become $3{\cdot}2 \times 10^3$, and strong absorption in this wave-length region would have been observed in the photographs of the vapour spectrum.

It thus appears that the absorption spectra here investigated have been correctly assigned to the two species ClO_3 and Cl_2O_6. It is of interest to note that ClO_3—unlike the other odd electron compounds, NO_2, ClO_2 and NO—exhibits continuous absorption. Furthermore, on polymerisation ($2ClO_3 \rightarrow Cl_2O_6$), the absorption is shifted toward the red end of the spectrum, whereas in the cases of NO and NO_2 the shift is toward the U.V.

The continuous nature of the spectrum of the trioxide indicates that the molecule dissociates on absorption of a light quantum. There are several possibilities as to the products but there is not sufficient evidence to decide between them.

The electronic absorption spectrum of ClO_3 does not give us any information as to its structure, but from a comparison with other tetratomic molecules a reasonable assumption can be made. Those possessing a total of twenty-six valence electrons, as in the cases of $(ClO_3)^-$, $(SO_3)^{2-}$, $(AsO_3)^{3-}$, $(BrO_3)^-$ and $(SbO_3)^{3-}$ are known to have stable pyramidal structures.[6] Similar molecules, with only twenty-four valence electrons, such as $(BO_3)^{3-}$, $(CO_3)^{2-}$ and $(NO_3)^-$ are symmetrically plane. Since ClO_3 possesses a total of twenty-five valence electrons its structure may lie somewhere between the pyramidal and planar forms.

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[6] W. H. Zachariasen, *J.A.C.S.*, 1931, **53**, 2123.

Summary.

Chlorine trioxide in the vapour phase has been found to absorb in the ultraviolet with a threshold at about 3500 Å. and two maxima at 2760 Å. and about 2000 Å. respectively.

Liquid chlorine hexoxide was investigated by means of a special quartz wedge cell and found to absorb strongly from about 6000 Å. throughout the whole of the spectrum to the limit of the spectrograph, 2200 Å.

The authors are indebted to the Department of Scientific and Industrial Research for a grant in aid of this research.

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London.

TRANSPORT NUMBERS OF UNSYMMETRICAL ELECTROLYTES AND A SIMPLIFIED MOVING BOUNDARY APPARATUS.

By G. S. Hartley and G. W. Donaldson.

Received 6th January, 1937.

The equations derived by Onsager[1] for the effect of Coulomb forces on the mobilities of ions in very low concentrations may be combined to give corresponding equations for the transport numbers. Thus, for aqueous solutions at 25° C.

$$\frac{dT_+}{d\sqrt{c}} \rightarrow \frac{21\cdot14}{\lambda}(Z_-T_+ - Z_+T_-)\sqrt{Z_+ + Z_-} \text{ as } c \rightarrow 0 \quad . \quad (1)$$

where T's are transport numbers, Z's numerical valences, λ the equivalent conductivity (ohm^{-1}cm.^{2} (gm. equiv.)$^{-1}$), and c the concentration (gm. equivs. per litre).

The uniunivalent electrolytes which have been the subject of very accurate measurements by MacInnes, Longsworth[2] and collaborators, show, except in the case of nitrates, qualitative agreement with equation (1) over the entire concentration range studied and reasonably good quantitative agreement below ·01N. Deviation from the limiting slope in higher concentrations is to be attributed to the decreasing validity of the approximations made in the derivation of the Onsager equation. The usual effect of hydration is to contribute another term of the same sign as (1), while association, since it affects both ions equally, has only a secondary effect on the magnitude of the slope.

In unsymmetrical electrolytes, the valences will usually determine the sign of the term in brackets in equation (1) and so of dT/dc. Unless the transport number of the univalent ion is less than one-third in a unibivalent electrolyte, or less than one-quarter in a unitervalent electrolyte, it will increase with increase of concentration. Association, since it would produce charged ion pairs, would have a direct effect on the transport numbers, and usually in the sense that that of the univalent ion would be reduced *—*i.e.*, in the opposite sense to the Onsager effect. This is, we believe, the only property on which the effects of Coulomb forces between free ions and of actual association of ions are of opposite sign.

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[1] Onsager, *Trans. Faraday Soc.*, 1927, **23**, 341.

[2] MacInnes and Longsworth, *Chem. Rev.*, 1932, **11**, 171 ; Longsworth, *J. Amer. Chem. Soc.*, 1935, **57**, 1185.

At the time this work was commenced, the most accurate data available for unsymmetrical electrolytes were those of Lucasse[3] (E.M.F. method) on calcium, strontium and barium chlorides and of Jones and Dole[4] (analytical method) on barium chloride. In all cases, dT/dc had the sign predicted by equation (1) even in very high concentrations. On the other hand, older measurements on sodium and potassium sulphates[5] suggested that there was little change of transport number with concentration. It was our object to obtain more accurate data for potassium sulphate, particularly in low concentrations, and then to examine two unitervalent salts. Since the work was commenced, further measurements, by Longsworth[2] (moving boundary method) on, i.a., calcium chloride and sodium sulphate, and by Jones and Prendergast[6] (analytical method) on lanthanum chloride, have appeared. The material available for comparison has thus been considerably increased, and we have taken the liberty of including these authors' data in the graph in Fig. 3.

Transport Number Measurements.†

These were made by the moving boundary method. With regard to marking and calibration of the boundary tube, optical arrangement for detecting the boundary by refractive index change, and correction for the conductivity of the water, the procedure of MacInnes and Longsworth[1] was followed. To bring the "leading" and "indicator" solutions into contact without serious mixing, the air bubble method used in the "balanced boundary" apparatus[7] was applied.

The apparatus for use with rising boundaries is shown in Fig. 1. The boundary tube A, of 7 mm. bore, is bent round at the top and sealed into the closed electrode vessel B, which is fitted with guard tubes as described by Drew and Hartley.[7] A is narrowed at the bottom over a length of 2 cm. to about 2 mm. bore and sealed into an oblique tube D, the right hand (descending) part of which is of capillary bore and bends up above the level of the thermostat water at E. The left hand part (ca. 5 mm. bore) bends up and round to the open electrode vessel C. A fine-bore capillary tube F is expanded at the bottom and sealed obliquely into the middle of the narrow part of A. To the end of F a short length of pressure tube with two screw pinch-cocks is attached. The apparatus is washed through and filled with leading solution with the upper pinch-cock closed and the lower one half open. After closing B and allowing time for thermal accommodation, the lower pinch-cock is compressed and the air column in F expands into the lower part of A and separates the solutions in A and D. By observing the "heel" of this foot-shaped air column G, leaks or volume change may be detected. The part CDE of the apparatus is then emptied by suction at the bottom of C and at E and washed through several times with water from C with suction at E. The suction at E is always arrested just before the receding meniscus in D reaches the junction with A, in order not to disrupt the air column. CDE is then filled with indicator solution, the electrode inserted in C and the voltage applied. The lower pinch-cock on F is now unscrewed till the air column has receded sufficiently to allow current to flow.

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* For example, formation of the ion-pair $K^+SO_4^-$ in potassium sulphate solution will merely reduce the mobility of the sulphate ion included in it, but will reverse the direction of the potassium ion included. On the other hand, only half as many equivalents of potassium as of sulphate are included in these ion pairs. It can be shown, however, in this case, that the resultant effect, in dilute solutions, will be to reduce the potassium transport number, unless the mobility of the ion pair is less than one-third that of the sulphate ion, which is extremely improbable.

[3] Lucasse, *J. Amer. Chem. Soc.*, 1925, **47**, 743.

[4] Jones and Dole, *ibid.*, 1929, **51**, 1073.

[5] See table in Kohlrausch and Holborn, *Das Leitvermögen der Elektrolyte*, Leipzig, 1916.

[6] Jones and Prendergast, *J. Amer. Chem. Soc.*, 1936, **58**, 1476.

† Experimental work by G. W. D.

[7] Hartley, Drew and Collie, *Trans. Faraday Soc.*, 1934, **30**, 648.

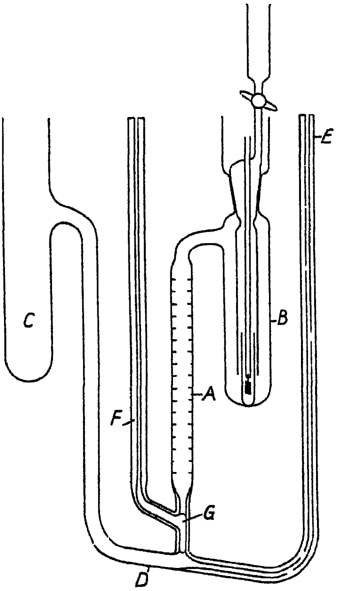

Fig. 1.

To avoid a tendency for solution to creep back into the lower part of F and cause a discrete bubble to separate which cannot be withdrawn, it was found to be necessary that—(1) the lower part of F should have a slightly *greater* bore than the lower part of A; (2) it should be sealed into A obliquely; (3) unnecessary expansion should be avoided during sealing, but the end of F should not be allowed to contract. When these conditions are fulfilled the air column is quite stable (at least with solutions of normal surface tension) in tubes of bore up to 3 mm.

This air-lock method is much simpler, both in operation and particularly in construction, than the shearing method developed by McInnes and Brighton[8] and used so successfully. Experiments with coloured solutions showed that the air-lock allowed no mixing of the solutions to occur, at least over a period of several hours, and caused very little disturbance when it was withdrawn. It is perfectly satisfactory in the ordinary moving boundary experiment, where it is not necessary for the boundary to be sharp initially, since it is actively sharpened and maintained sharp by the current.[9] It is, however, necessary that none of the leading electrolyte should be left behind the boundary in a region through which no current flows, so that it can escape by diffusion only, and for this reason the air column is at first only withdrawn sufficiently to permit current to pass. It is withdrawn into the tube F itself when the boundary is about 2 cm. down the tube.

The apparatus for falling boundaries was used only with higher concentrations ($> N/20$) and the boundary tube was, therefore, of narrower bore (about 3 mm.). In the apparatus with which the measurements here recorded were made, a discrete air bubble was used to keep the solutions separate. This was controlled by flow through the tap on the reservoir attached to the closed electrode vessel (corresponding to H, Fig. 1). Although very satisfactory results were obtained, the protruding air-column used in the rising boundary apparatus is more easily controlled and testing for leaks in this apparatus is more certain since no operation on the closed electrode vessel is necessary between the test and the measurement. The falling boundary apparatus used in these experiments has, therefore, now been replaced by an apparatus similar in principle to the rising boundary apparatus. It is this new apparatus which has been used by Mr. Samis for the measurements reported in the following paper. It may be described with reference to Fig. 1: C becomes the closed electrode vessel, B being open: D and A are connected by a plain bend, and the *upper* part of A is narrowed and has the tube F sealed into it: tube E becomes an extension of the tube joining A to B. The air column forced into the top of A through F in this case expands upwards.

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[8] MacInnes and Brighton, *J. Amer. Chem. Soc.*, 1925, 47, 994.

[9] For this and other principles in the theory of the measurement, see MacInnes and Longsworth[3]; and Hartley and Moilliet, *Proc. Roy. Soc. A*, 1933, 140, 141.

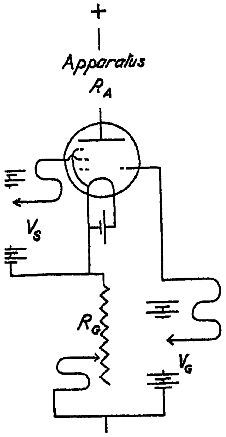

FIG. 2.

Each apparatus was constructed in Pyrex and strengthened by mounting in an oak clamp. The latter was fitted with three levelling screws which rested on an angle-iron frame which did not touch the thermostat but was fixed rigidly to a main brick wall.

A thermionic valve circuit was used to maintain a constant current. This is very much simpler than the photo-cell-controlled mechanical device of MacInnes and collaborators [10] and we think adequate when the highest possible precision, is not desired. The moving boundary apparatus was placed in the anode circuit of an ordinary 2 volt pentode output valve (Marconi PT2). The filament was heated by means of a large capacity accumulator and the screen grid was given a steady bias V_S by means of an ordinary HT dry-cell (see Fig. 2). The control grid receives automatic bias by means of the resistance (a plug box) R_G, largely backed out by a suitable voltage from the dry-cell V_G. The potential V was the 220 volts of the D.C. mains augmented when necessary by dry-cells in series. A simple calculation gives

$$\left\{\frac{\delta \log I_A}{\delta \log R_A}\right\}_V = \frac{R_A}{R_A + \rho + (M + 1)R_G} \quad . \quad . \quad . \quad (2)$$

where R_A is the apparatus resistance, ρ is the slope resistance of the valve and M is the amplification factor. These are approximately 300,000 ohms. and 1000. For a $N/10$ solution R_A is of the order of 100,000 ohms. If R_G is made equal to 10,000 ohms, then it follows that a 20 per cent. change of the apparatus resistance will produce only a 0·01 per cent. change of current. I_A is also insensitive to changes of supply voltage. In practice, slow change of filament emission seems to set a limit to the constancy that can be obtained. With currents between 0·5 and 4 mA, the current drifted during an experiment by about 1 part in 500. With smaller currents, the constancy was less satisfactory. The residual change of current was a steady drift, which was allowed for in calculating the results. The measurement was made by including, in series with the transport apparatus, a standardised resistance box, in parallel with which a galvanometer and Weston cell could be connected. A milliameter was also included for convenience when setting the values of V_S, V_G and R_G for the desired current.

It is essential that the electrode on the closed side should not permit evolution of gas and that the reaction, if the electrode is a cathodes should not give rise to anions (or if anode to cations) more mobile than those of the solution under investigation. The electrode in the closed vessel was of fine platinum gauze heavily silver plated. The second apparatus was fitted with standard ground joints so that alternative electrodes were available.

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[10] MacInnes, Cowperthwaite and Blanchard, *J. Amer. Chem. Soc.*, 1926, 48, 1909.

When required as a cathode, the silver was converted to chloride electrolytically. The silver anode in potassium ferricyanide solution formed a precipitate and coating of silver ferricyanide. In the sulphate solution it dissolved giving rise to silver ions, but these are less mobile than potassium. The silver chloride cathode formed chloride ions in all cases, but these are less mobile than either sulphate or ferricyanide.

Gassing at the electrode in the open vessel is of no consequence if the hydrogen or hydroxyl ions produced are neutralised. Except when using methylene blue (chloride) as indicator, when a silvered gauze electrode was used, the electrode in the open vessel was a plain platinum wire. When lithium ion was used as indicator, solid lithium carbonate served to remove the hydrogen ions, and when acetate or permanganate was used, the corresponding acid was added in solution. A system of guard tubes forced the current to pass through the alkaline or acid region and prevented dispersal of the added solute by convection.

It is not in general necessary for the original " indicator " solution to have an ion in common with the leading electrolyte, because, in the synthetic " Kohlrausch " solution, formed behind the boundary as it advances, this ion is supplied by the leading electrolyte. Thus we may start with LiCl above K_2SO_4; in the Kohlrausch solution, which is the actual indicator, Li is supplied from the former and SO_4 from the latter. The only restriction is the avoidance of an unstable density difference. For example, we could not use LiCl above K acetate with positive current flowing downwards, because, in addition to the descending boundary between K acetate (heavier) and Li acetate (lighter), there would be an ascending boundary between LiCl (heavier) and Li acetate (lighter). The density difference would render the latter unstable and the resulting convection might disturb the other boundary. Corresponding trouble does not arise when LiCl is used above K_2SO_4 or $K_3Fe(CN)_6$, as a second ascending boundary is not formed, the following radical being in each case the faster, and the diffuse transition is stable because the sulphate or ferricyanide solution is heavier than the chloride at a corresponding concentration. Stabilisation of the solution above a descending boundary was further assured by starting with the original upper solution less concentrated (10-20 per cent.) than the calculated Kohlrausch concentration $C_X{}^K$, which is given by the Kohlrausch equation :—

$$\frac{C_X{}^K}{T_X{}^K} = \frac{C_R}{T_R} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

R being the leading radical, X the following radical, C's concentrations and T's transport numbers, superscript K denoting the Kohlrausch solution. In working with a rising boundary, the original indicator concentration was made greater than the Kohlrausch concentration.

With the exception of methylene blue, which was a specially purified specimen for which we are indebted to Dr. Conmar Robinson and Mr. H. E. Garrett, and of lithium chloride, which was prepared in solution with a deliberately alkaline reaction by dissolving pure lithium carbonate in redistilled hydrochloric acid, the salts used were B.D.H. products, of " Analar " quality when obtainable, recrystallised from conductivity water. The lithium carbonate was obtained from the nitrate, a trace of calcium in which was first removed by precipitation with ammonium oxàlate, by precipitating a concentrated solution with ammonium carbonate and washing the precipitate in hot water. Solutions were made up by volume at 25° C. Conductivities of solutions made up from the original and recrystallised materials showed satisfactory agreement.

Solutions of concentration greater than $N/20$ were investigated in the falling boundary apparatus and the position of the boundary determined by the refractive index change. More dilute solutions were investigated in

TABLE I.—TRANSPORT NUMBERS AT 25° C.

Electrolyte and Concentration. (Equivs /Litre.)	Original "Indicator," Electrode in Closed Vessel, and Type of Boundary.	Observed Transport Number.	Volume Change Correction.	Water Correction.	Corrected Cation Transport Number.
KCl.					
0·1000	LiCl AgCl Falling	cation 0·4902	0·0002		
0·1000	KAcetate Ag Falling	anion 0·5104	0·0002		0·4894
0·01000	$KMnO_4$ Ag Rising	anion 0·5100		+ 0·0003	0·4897
0·01000	MeBlue AgCl Rising	cation 0·4898		+ 0·0003	0·4901
0·00000					0·4906
K_2SO_4.					
0·5000	LiCl AgCl Falling	cation 0·4891	+ 0·0018		0·4909
0·2000		0·4904	+ 0·0006		0·4910
0·1000		0·4886	+ 0·0004		0·4890
0·0500		0·4868	+ 0·0002		0·4870
0·02000	$KMnO_4$ Ag Rising	anion 0·5155	— 0·0005	+ 0·0002	0·4848
0·01000		0·5170	— 0·0002	+ 0·0003	0·4829
0·00500		0·5176	— 0·0001	+ 0·0007	0·4818
0·00250		0·5197		+ 0·0014	0·4789
0·00000					0·477
$K_3Fe(CN)_6$.					
0·1000	LiCl AgCl Falling	cation 0·4431	— 0·0017		0·4414
0·0500		0·4398	— 0·0008		0·4390
0·1000	KAcetate Ag Falling	anion 0·5570	+ 0·0024		0·4406
0·0500		0·5604	+ 0·0012		0·4384
0·01000	MeBlue AgCl Rising	cation 0·4314	— 0·0002	+ 0·0003	0·4315
0·00000					0·422
$Co(NH_3)_6Cl_3$.					
0·0500	LiCl AgCl Falling	cation 0·5641	+ 0·0006		0·5647
0·01000	$KMnO_4$ Ag Rising	anion 0·4324		+ 0·0003	0·5673
0·00000					0·572

the rising boundary apparatus using a coloured indicator ion. The boundary was timed by means of an accurate clock whose face was graduated on the metric system with minute units and could be read if necessary to 0·02 minute. It was found, however, difficult to fix the time at which the boundary passed each mark on the tube more closely than permitted a possible error, as between one mark at the top of the tube and one at the bottom, of 0·3 per cent. The boundary was timed between different pairs of marks at the top and bottom. The average figures for different experiments at the same concentration agreed to within 0·2 per cent. except in a few cases, where too great a current had been used or in which slight gassing had occurred either at the electrode or due to insufficient de-aeration of the solution before filling. At most concentrations, measurements were made with different currents and values in the range of current where the observed transport number increased with increase of current were discarded. Timing the boundary at intermediate marks on the tube gave a check on the constancy of its velocity and where this was not within the limits of accuracy of timing the results of the experiment were discarded.

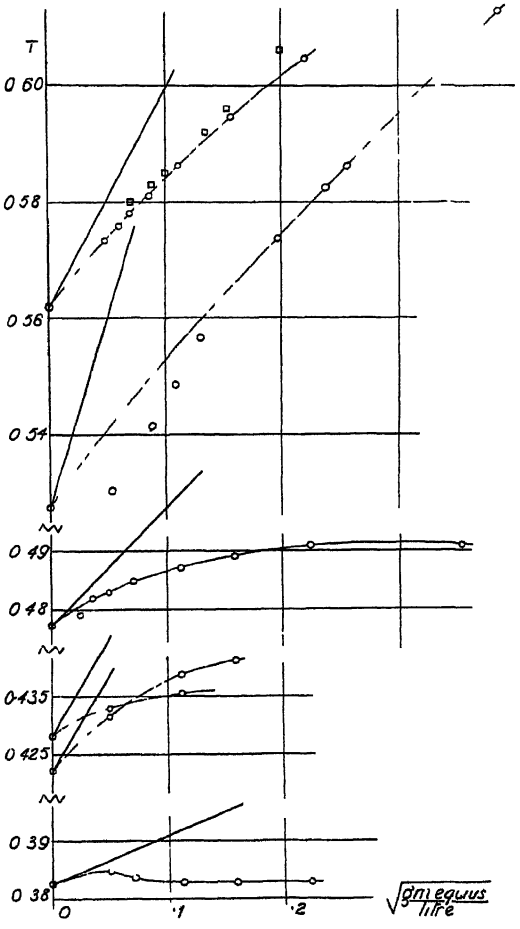

FIG. 3.—Transport numbers of univalent radical in several unsymmetrical electrolytes at 25° C. $CaCl_2$ and Na_2So_4 from Longworth.[2] $CaCl_2$ (□) from Lucasse.[3] $LaCl_3$ from Jones and Prendergast.[6] K_2SO_4, $K_3Fe(CN)_6$ and $Co(NH_3)_6Cl_3$ from present work.

Ammonia-free conductivity water was used. As no attempt was made to exclude atmospheric carbon dioxide from the apparatus, the actual solvent conductivity for correction purposes was taken to be that of "equilibrium water," *i.e.* $1{\cdot}0 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$. The equivalent volumes necessary for calculation of the volume change correction were calculated from density data. The density of solid silver ferricyanide was measured and found to be 3·10. Densities of hexamine cobalt chloride solutions were taken from the works of Harkins, Hall and Roberts,[11] and other densities from the

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[11] Harkins, Hall and Roberts, *J. Amer. Chem. Soc.*, 1916, 38, 2643.

International Critical Tables. Where the electrode reaction gave rise to a third kind of ion, it was assumed that the partial volumes of the salts present were the same as in pure solutions of the same ionic strength. The volume correction is not exact, since the concentration in the neighbourhood of the electrode is not exactly known and the densities of electrolytically deposited metals and salts are rather variable.[12] The total correction, however, in the least favourable case, amounted only to ·002, and the uncertainty introduced must be well within the ·2 per cent. introduced in the measurements themselves.

The results are collected in Table I. Each value is the average of several determinations. Measurements were made on potassium chloride in order that, by comparison with the extremely accurate determinations of MacInnes, Longsworth [3] and collaborators, the satisfactory working of our apparatus could be confirmed. In some cases, determinations were made using both cationic and anionic boundaries, making use of the relationship $T_+ + T_- = 1$, since the agreement of these measurements is a very useful check on accuracy. The infinite dilution values were obtained from the conductivity work described in the next section, using the accurate values of MacInnes, Shedlovsky and Longsworth [13] for the infinite dilution conductivities of the K and Cl ions (73·5 and 76·3 respectively).

The data are plotted against square root of concentration in Fig. 3. The heavy lines are the limiting slopes derived from equation (1), the values of the coefficient of the square root of concentration for potassium sulphate, potassium ferricyanide and hexamine cobalt chloride being 0·102, 0·167 and 0·166 respectively.

Conductivity Measurements.*

The infinite dilution values of the equivalent conductivities of the three salts investigated could not be obtained with sufficient accuracy by extrapolation of published data and measurements were, therefore, made in extremely dilute solutions.

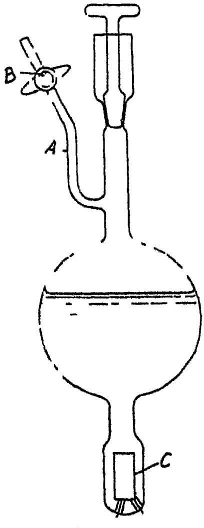

Fig. 4.

The cell (Fig. 4) was one which permitted measurements to be made without contact of the solution with ordinary air. A supply of air (at about 6 cm. of water pressure) from which carbon dioxide and ammonia had been removed by washing with acid and concentrated alkali, was connected to the side-tube, A, whenever it was necessary to remove the stopper of the vessel. The tap on this tube had a groove B cut in the barrel so that the upper part of the tube was swept out before opening the tap. The tap was always opened before the stopper was removed and closed after it was replaced. There was thus always an outward current of pure air in the neck of the vessel whenever this was open. At the commencement of the experiments, the vessel was first weighed dry and then filled with pure water. It was then slowly emptied by partial rotation in (for the position shown) a clockwise direction, so that the water was displaced by purified air supplied through the side tube. This operation was several times repeated and then about 250 c.c. of pure water introduced, and the stopper, lightly greased, inserted. After reweighing, placing in the thermostat and allowing time for temperature accommodation, the conductivity was measured. The

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[12] Smith, *Bureau of Standards Journal of Research*, 1932, 8, 457.

[13] MacInnes, Longsworth and Shedlovsky, *J. Amer. Chem. Soc.*, 1932, 54, 2758.

[* Experimental work by G. S. H.]

TABLE II.—EQUIVALENT CONDUCTIVITIES AT 25° C.

Each group of figures represents one series of dilutions.

The values at $\sqrt{c} = 0{\cdot}0500$ are intrapolated from measurements in the higher resistance cell. The infinite dilution values were obtained by graphical extrapolation, using the theoretical value for $\frac{d\lambda}{d\sqrt{c}}$.

$\sqrt{\text{gm. eq./litre}}$	λ.	$\sqrt{\text{gm. eq./litre.}}$	λ.	$\sqrt{\text{gm. eq./litre.}}$	λ.	$\sqrt{\text{gm. eq./litre.}}$	λ.
KCl.*		**$K_3Fe(CN)_6$.**		**K_2SO_4.**		**$Co(NH_3)_6Cl_3$.**	
0·0500	145·35	0·0500	157·1	0·0500	143·7	0·0500	158·3
0·0000	149·82	0·0000	174·4	0·0000	154·3	0·0000	178·2
0·00581	149·3	0·00602	172·4	0·00510	153·3	0·00383	177·0
0·01125	148·7	0·01194	170·4	0·00999	152·3	0·00774	175·7
0·01704	148·2			0·01486	151·3	0·01162	174·2
0·02260	147·75	0·00595	172·5	0·02426	149·1	0·01530	172·7
		0·01181	170·5				
0·00488	149·4	0·01664	168·7	0·00899	152·5	0·00466	176·8
0·00975	148·9			0·01106	152·0	0·01560	172·5
0·01947	148·0	0·00574 †	172·5	0·01330	151·6		
		0·01359 †	169·8	0·01759	150·6		
0·01130	148·8					0·00450 ‡	176·7
0·02420	147·6	0·00643 †	172·3	0·00448	153·4	0·00617 ‡	176·2
		0·00903 †	171·4	0·01107	152·0	0·01153 ‡	174·3
		0·01928 †	167·7	0·01982	150·1	0·01530 ‡	172·8
				0·02201	149·6		
						0·00472 ‡	176·8
						0·01186 ‡	174·3
						0·01944	171·3

* Value at $\sqrt{c} = 0{\cdot}0500$ obtained from Shedlovsky's data and used for calibration of cell. The dilution cell calibrated by fitting all observed data as closely as possible to Shedlovsky's extrapolation.

† In water containing HCN at concentration of $2 \times 10^{-4}N$.

‡ In water containing NH_3 at concentration of $10^{-6}N$.

measurement was repeated, stirring the water in between by completely inverting the vessel several times, until consistent readings were obtained. The salt was added in the form of a stock solution of about $N/20$ concentration from a small weight pipette. After each addition, the stirring process was repeated till consistent resistance readings were obtained. Several successive additions were made in the course of each experiment. In washing the cell in between experiments it was not necessary to fill the cell completely as was done at the commencement of the whole series. In this work, water of specially good quality was used, and any filling which had a specific conductivity higher than $0{\cdot}15 \times 10^{-6}$ was rejected. The value was usually between $0{\cdot}10$ and $0{\cdot}11 \times 10^{-6}$ ohm^{-1} cm^{-1}.

To test the efficiency of the method of preventing access of carbon dioxide an experiment was made in which the operations of adding solution were several times carried out but without actually making any addition. No appreciable rise of conductivity resulted. A slight rise of conductivity with time, due presumably to slow solution of the glass (Jena " Normal "), took place, but was not great enough to make correction for it necessary. The stock solutions were made up in pure water which had been allowed to come to equilibrium with atmospheric carbon dioxide and a correction was, therefore, made for the carbon dioxide transferred to the conductivity vessel when stock solution was added. The magnitude of this small correction was determined by an experiment in which successive additions of "equilibrium water" alone were made to the pure water in the vessel. The specific conductivity of the original water plus the additional conductivity due to the introduction of carbon dioxide with the stock solution was subtracted from the specific conductivity of each solution.

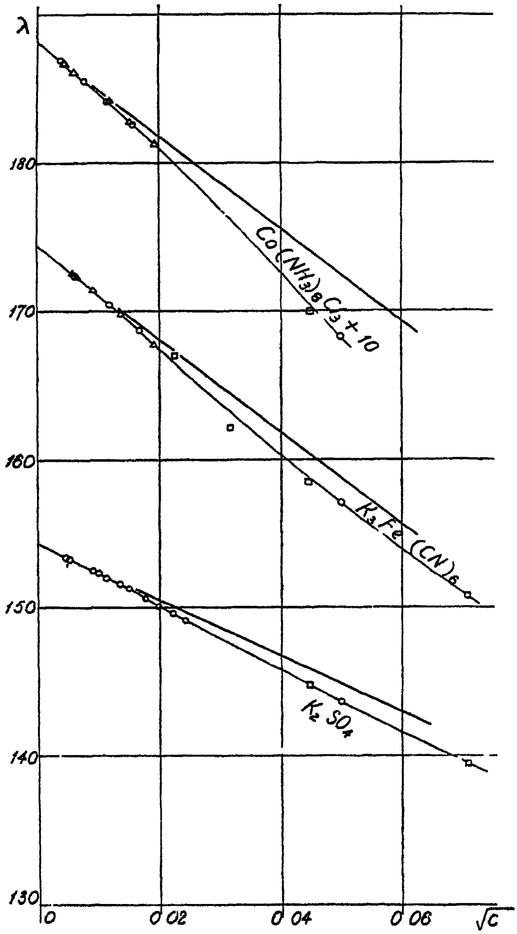

FIG. 5.—Equivalent conductivities at low concentrations.

□ ($Co(NH_3)_6Cl_3$), data of Harkins, Hall and Roberts.[12]

□ ($K_3Fe(CN)_6$), data from I.C.T.

□ (K_2SO_4), data of Noyes and Falk.[16]

○ Present work, using pure water.

△ Present work, with addition of NH_3 (in the case of $Co(NH_3)_6Cl_3$) or HCN (in the case of $K_3Fe(CN)_6$).

The electrodes C, connected in the usual way by mercury-filled side-tubes (not shown), were coaxial cylinders of smooth platinum (0·1 mm. thick), fixed at several places by short glass rods. They were contained in an extension (about 15 c.c. capacity) of the main vessel, so that the resistance was independent of the total amount of solution, provided that the electrode vessel itself was completely filled. Resistance measurements were made on a six-dial decade non-inductive resistance box (0·1 to 10,000 ohms per coil). Fixed equal ratio-arms were used throughout, a shunt being necessary across the cell when water was being measured, and alternating potential (ca. 0·5 volt) was supplied across the ratio arms from a valve oscillator, giving frequencies of 1000, 1000$\sqrt{2}$ and 2000 cycles per second. The common point of the cell (outer electrode) and variable resistance was directly earthed. The detector was a tuned two-valve amplifier and headphones. By commutating the oscillator-bridge connections for each measurement and taking the mean of the readings, errors due to direct earthing were (for equal ratio) eliminated. The correction necessary for non-ideal capacity in the leads to the cell was determined, for each frequency, by calibration with a standard resistance box in the cell position. By working with the outer electrode, and thermostat, earthed, error due to resistance-and-capacity-in-series shunts was greatly reduced. The small residual error, appreciable only at the lowest concentrations used, was eliminated by extrapolation against square of frequency to zero frequency. The cell was not used for concentrations higher than 5 × 10^{-4} *N*, since, above this concentration, the increase of compensating capacity with decreasing frequency indicated that the polarisation error, which cannot be exactly eliminated, was appreciable.

The stock solutions were made up by weight. Their concentrations were checked by diluting by weight to approximately *N*/400 with " equilibrium " water and measuring the conductivities of the diluted solutions. For comparison, the values of the equivalent conductivity were corrected to the concentration of exactly *N*/400 using values for the rate of change of equivalent conductivity with square root of concentration obtained from published data. The values obtained were always in agreement within 0·1 per cent.

Both cells used were calibrated by experiments with potassium chloride solutions, using the data and extrapolation of Shedlovsky.[14]

In the case of the alkaline earth chlorides [15] the actual equivalent conductivity-square root of concentration curve approaches the limiting slope derived from Onsager's equation in a regular manner from above, as in the majority of uniunivalent electrolytes. Onsager,[1] however, using the data of Kohlrausch at 18°, found that for potassium sulphate the deviation is at first in the opposite sense. Our measurements confirm this behaviour (Fig. 5) and the two unitervalent electrolytes show the same behaviour in more marked degree. Direct evidence against an appreciable fraction of the conductivity of either of the unitervalent electrolytes being due to hydrolysis was obtained in the following way. Hydrolysis of the ferricyanide ion would take place according to one of two equations,

$$[\mathrm{Fe(CN)_6}]^{\equiv} + 2\mathrm{H_2O} \rightarrow [\mathrm{Fe(CN)_5\,H_2O}]^{=} + \mathrm{HCN} + \mathrm{OH}^{-}$$

or $$[\mathrm{Fe(CN)_6}]^{\equiv} + \mathrm{H_2O} \rightarrow [\mathrm{Fe(CN)_5\,OH}]^{\equiv} + \mathrm{HCN}$$

or some combination of these. Further co-ordinated cyanide ions might be similarly replaced. Both processes give rise to the almost completely undissociated hydrocyanic acid. By addition of this substance to the water used in the conductivity measurements, the hydrolysis would therefore be suppressed without seriously increasing the residual conductivity of the solvent. In two of the four experiments on potassium ferricyanide the water was made approximately 2 × 10^{-4} *N* in HCN by addition of redistilled acid (2 per cent. solution, B.P.). The solvent conductivity was thereby increased to about 0·21 × 10^{-6} $\mathrm{ohm^{-1}\,cm^{-1}}$, but the conductivity of the salt, even at the lowest concentration used was not changed by more than the experimental error, when allowance was made for a peculiar time effect to be described below. In the case of hexamine cobalt chloride, hydrolysis of the type

$$[\mathrm{Co(NH_3)_6}]^{+++} + \mathrm{H_2O} \rightarrow [\mathrm{Co(NH_3)_5H_2O}]^{+++} + \mathrm{NH_3}$$

might take place, and, if so, the ammonia produced would,in the very low concentration in which it would be present, be extensively ionised. In this case a very small quantity of dilute ammonia solution was added to the water used in two of the experiments, making it approximately 10^{-6} *N* in total ammonia, having a conductivity of about 0·24 × 10^{-6} $\mathrm{ohm^{-1}}$ $\mathrm{cm.^{-1}}$. The conductivity of the salt was again unchanged.

Slow hydrolysis does indeed occur in potassium ferricyanide solutions, since they deposit ferric hydroxide if left standing for a considerable time. No measurements recorded on this salt were made in solutions more than eight hours old. During this time the conductivity of the solution *in bulk* did not change appreciably and one solution of concentration about

[14] Shedlovsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1405.

[15] Shedlovsky and Brown, *ibid.*, 1934, **56**, 1066.

[16] Noyes and Falk, *ibid.*, 1911, **33**, 1436.

3×10^{-4} N showed only 2 per cent. increase of conductivity over a period of three weeks. It must be remembered, however, that hydrolysis according to the second equation given would probably cause little change of conductivity. There was, however, a considerable time effect on the solution in immediate contact with the electrodes. After the temperature of the conductivity vessel had accommodated to that of the thermostat, a steady *fall* of conductivity persisted when no hydrogen cyanide had been added to the solution, while in the solutions to which hydrogen cyanide had been added, there was a steady *rise* of conductivity. After stirring the contents of the vessel, so that the solution in contact with the electrodes was changed, the behaviour was repeated. Extrapolating the resistance against time back to the time of stirring (taking into consideration only the readings in the period of steady change, after thermal equilibrium had been established) concordant values were obtained. There was, therefore, no appreciable effect in the bulk of the solution, and one must conclude that some reaction takes place on the surface of the platinum.

Discussion.

The infinite dilution values for the equivalent conductivities of the three salts investigated lead to values for the $SO_4^{=}$, $Fe(CN)_6^{\equiv}$ and $Co(NH_3)_6^{\ddagger}$ ions of 80·8, 100·9 and 101·9 respectively. The value for the $SO_4^{=}$ ion is somewhat higher than that (79·7) taken by Longsworth [2] on the basis of some preliminary measurements by Shedlovsky on Na_2SO_4. Our value for the $SO_4^{=}$ ion gives T_+° in $Na_2SO_4 = 0{\cdot}3827$ in place of Longsworth's 0·3859, and if the former value is taken (as on the graph in Fig. 3), there is direct experimental evidence that dT_+/dc for this salt is at first positive.

For all the other salts, dT/dc for the univalent radical is positive over a much greater range of concentration, and the results are, therefore, in qualitative agreement with Onsager's theory. The absolute deviations of the experimental data from the values on the limiting slope at any one concentration decrease in the order $CaCl_2$, K_2SO_4, Na_2SO_4. The ratios of the actual to the limiting theoretical values of $dT/d\sqrt{c}$, however, also decrease in this order, as do the $dT/d\sqrt{c}$ values themselves. There is, therefore, in the absence of any knowledge of the probable effect of higher order concentration terms in the Onsager theory, insufficient difference in behaviour between these three salts to permit any conclusions to be drawn about differences in tendency to form ion-pairs. That dT/dc is negative over a certain range in Na_2SO_4, and perhaps also in K_2SO_4, suggests, however, that ion-pair formation is appreciable.

With regard to the unitervalent salts, the deviations of the observed transport numbers from the limiting slope are all greater, as would be expected, than in the unibivalent. The limiting slopes for $K_3Fe(CN)_6$ and $Co(NH_3)_6Cl_3$ are almost identical, and the considerable difference in the actual slopes may, therefore, be due to more extensive ion-pair formation in the latter salt.

If the conductivity data of Jones and Bickford [17] for $LaCl_3$ are extrapolated by means of the theoretical slope, 144·6 is obtained for the infinite dilution value. The corresponding T_-° value, 0·5275 has been plotted on the graph. This is considerably higher than the value, 0·513, obtained by Jones and Prendergast [6] by extrapolation of their transport data. It is consequently not in good agreement with the transport data in the lowest concentrations, but it seems to us more likely that it is the latter, which do not in any case follow very smoothly on the data for higher concentrations, which are in error. If Jones and Prendergast's extrapolation is taken as correct, the deviation of the observed transport numbers from the limiting slope is smaller than that of the other unitervalent salts. Jones and Bickford's conductivity data, on the other hand, show a much *greater* deviation than is found in K_2SO_4, $K_3Fe(CN)_6$, or $Co(NH_3)_6Cl_3$ and of the same type.

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[17] Jones and Bickford, *J. Amer. Chem. Soc.*, 1934, **56**, 206.

Summary.

A simplified type of accurate moving boundary apparatus has been described, and measurements on three unsymmetrical electrolytes are recorded.

Conductivity measurements have been carried out in very low concentrations of K_2SO_4, $K_3Fe(CN)_6$ and $Co(NH_3)_6Cl_3$, and the values of 80·8, 100·9 and 101·9 established for the infinite dilution conductivities of their multivalent ions at 25° C.

The transport numbers of unsymmetrical electrolytes are shown to change with concentration, in low concentrations, in the direction predicted by the Onsager theory. Deviations from the theory occur with increase of concentration and in all cases in the sense that the actual change of transport number is less than the theory predicts.

One of us (G. W. D.) is indebted to the Order of Daughters of the Empire (Canada) for a scholarship which enabled him to take part in this research.

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THE TRANSPORT NUMBERS OF SOME SALTS IN AQUEOUS SOLUTION AT HIGHER TEMPERATURES.

By C. S. Samis.

Received 6th January, 1937.

This communication is concerned with the determination of the transport numbers at various concentrations of certain salts in aqueous solution at 40° and 50°. These data were required primarily in connection with research carried out in this laboratory on colloidal electrolytes.

They were, however, considered to be of general interest since very little work has been carried out upon the transport numbers of salts at temperatures higher than 25°, and only for this temperature are any accurate data available.

From Longsworth's data[1] on KCl at 25° and our data on the same salt at 40° we have obtained the temperature coefficient for the ions of KCl, which formerly rested upon assumption.[2] Hence the mobility at infinite dilution for a number of ions may be calculated with greater accuracy from the equivalent conductivity at infinite dilution of their salts at higher temperatures.

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[1] Longsworth, *J. Amer. Chem. Soc.*, 1932, 54, 2741.

Apparatus.

The falling boundary apparatus described by Hartley and Donaldson,' fitted with the air-lock mechanism used in their rising boundary apparatus and subject to some minor modifications, was used in making the measurements recorded in this paper. The relatively large 300 c.c. electrode vessel was replaced by a smaller 150 c.c. vessel with a standard ground joint. The volumes between the graduations No. 1 and 21, 2 and 20, 3 and 19, 4 and 18, 5 and 17 were calibrated by means of a KCl — LiCl falling boundary at 25°, using the K^+ ion transport number data of Longsworth.[1] The volume between 1 and 21 determined by this method agreed very well with the volume obtained by Donaldson using the mercury method.[4]

Materials.

" Analar " potassium chloride, potassium oxalate and silver nitrate were used. Pure LiCl was prepared as described by Hartley and Donaldson.[3] The hydrogen chloride solutions were prepared from redistilled pure acid. All the other chemicals were pure materials obtained from Kahlbaums, Hopkin and Williams and B D.H.

The precipitates * of Zn(OH)Br, which the $ZnBr_2$ solutions contained, were not removed. The concentrations of all the solutions were determined from conductivity measurements made upon them at 25°, using the data of Shedlovsky [6] with the exception of the $ZnBr_2$ and K oxalate solutions, which were determined by direct analysis. The concentrations at higher temperatures were corrected for thermal expansion. All indicator solutions were made up to a concentration less than the calculated Kohlrausch value. Both LiCl and $LiNO_3$ were used as indicators and found to give identical results.

Experimental.

The concentration range covered by means of a refractive index boundary alone was roughly from 0·03 to 0·2 normal, but below 0·03 it was found necessary to use coloured indicators.

In some cases the observed transport number was found to vary with the current, but this variation becomes insignificant with suitably low currents. The observed values recorded here were obtained in this lower current range.

In the experiments with HCl this current was so low that the boundary could not be observed, and it was necessary to add acid methyl orange † to the HCl solution in order to produce a change in colour, as the boundary progressed. Since acid methyl orange is zwitterionic it can contribute no conductivity itself and is not likely to modify appreciably the conductivity of the HCl solutions. Actually there was no difference in the observed conductivity of the HCl solutions before and after the addition of the salt. For the determination of the transport number in 0·01 N solution of $ZnBr_2$, di-methyl aniline azo p-benzyl trimethylammonium nitrate was used as an indicator, since methylene blue failed to give a satisfactory boundary. In this case it was observed that the zinc which deposited upon the electrode reacted with the water. In order to overcome this "gassing" a mercury electrode was utilised with which the zinc amalgamated. All the transport number data recorded in this paper were obtained from falling boundaries. The observed values are given in Table IV.

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[2] Johnson, *J. Amer. Chem. Soc.*, 1909, **31**, 1015.

[3] Hartley and Donaldson, this volume, p. 457.

[4] MacInnes, *Chem. Reviews*, 1932, **11**, 171.

[5] *Arch. Chem. Farm.*, 1935, **2**, 237.

* p_H measurements on the aqueous solutions of $ZnBr_2$ show negligible hydrolysis, indicating that $ZnBr_2$ is analagous to $ZnCl_2$[5], where the difference in ($ZnCl_2$) between filtered and unfiltered aqueous $ZnCl_2$ solutions containing suspended Zn(OH)Cl is 0·02 per cent.

[6] Shedlovsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1911.

† The concentration of the methyl orange was roughly 3×10^{-5} *N*.

The density data in I.C.T. were used to determine the partial equivalent volumes of each salt and the equivalent volumes of the solids for the calculation of the volume correction. All the concentrations are expressed in gram equivalents per litre of solution at 40° or 50° as indicated.

The transport number limiting slope required by the interionic attraction theory is given by the equation

$$T_+ = T_+{}^\circ + \frac{\beta}{\lambda_0}(Z_+T_- - T_+Z_-)\sqrt{Z_- + Z_+}\sqrt{C}$$

where β has the value of 29·0 at 40° and 35·1 at 50°.

No equivalent conductivity measurements were made in this research; the data on the equivalent conductivity given in Table I. and II. were obtained from the published work of the authors, to whom references are made. The value of the infinite dilution equivalent conductivity of KCl at 50° was obtained by extrapolating by means of the limiting slope all the available data on the conductivity of KCl at 50°.

TABLE I.

	KCl.	K Oxalate.	HCl.	$ZnBr_2$.	$AgNO_3$.
$\lambda_{50}{}^\circ$.	230·5 [hb]	232·0 [a]	580·6	218	203·9 [g]
$T_{25}{}^\circ$.	0·4906 [j]	0·4933 [c]	0·8210 [j]	0·3830	0·4643 [e]
$T_{40}{}^\circ$.	0·4913	0·4913	0·8178	0·4100	0·4717
$T_{50}{}^\circ$.	0·4917	0·4883	0·7981	0·4280	0·4768

TABLE II.

	KNO_3.	KBr.	HNO_3.	$ZnNO_3$.	K Oxalate.
$\lambda_{50}{}^\circ$.	220·0 [a]	238 [d]	570 [b]	200 [e f]	232 [a]
$\lambda_{25}{}^\circ$.	—	—	—	119 [e f]	149 [a]

[a] Johnson, *J.A.C.S.*, 1909, **31**, 987.
[b] Noyes, *J. Physic. Chem.*, 1908, **6**, 505.
[c] Longsworth, *J.A.C.S.*, 1935, **57**, 1185.
[d] Gropp, *Dis. Rostock*, 1915.
[e] Jones, *et al.*, *Proc. Carnegie Inst.*, 1912, 176.
[f] Noyes, *ibid.*, 1907, **63**, 105.
[g] Kohlrausch and Holborn, *Das leitvermögen der Electrolyte*, Leipzig, 1916.
[h] *I.C.T.*, vol. IV., page 234.
[j] Longsworth, *J. Amer. Chem. Soc.*, 1932, **54**, 2741.

The observed transport number values for the K and Cl ions in KCl at 40° were plotted and extrapolated to infinite dilution by means of the limiting slope at 40°. The value of $T_+{}^\circ$ for the K ion thus obtained was 0·4913 ∓ 0·0003. From this value of $T_+{}^\circ$ and Longsworth's value of $T_+{}^\circ$

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[7] Davies, *The Conductivity of Solutions*, page 196, 1930.

TABLE III.

	H^+.	Zn^{++}.	K^+.	NO_3^-.	Br^-.	Cl^-.
l_{50}° .	463·3	93·2	113·4	106·7	124·8	117·1

TABLE IV.

Electrolyte. Gram Equiv./l. At Temp. Given.	(1) Original Indicator. (2) Electrode in Closed Vessel.	Observed Transport Number.	Volume Change Correction.	Corrected Cation Transport Number.
KCl 40°.				
0·09945	LiCl Ag-AgCl	T^+ 0·4903	− 0·00024	0·4901
0·09945	K Valerate Ag	T^- 0·5089	+ 0·00024	0·4908
0·1490	LiCl Ag-AgCl	T^+ 0·4910	− 0·00049	0·4905
0·1983	LiCl Ag-AgCl	T^+ 0·4907	− 0·00074	0·4900
0·1983	K Valerate Ag	T^- 0·5096	+ 0·00074	0·4896
K Oxalate 40°.				
0·04976	K Valerate Ag	T^- 0·5038	− 0·0001	0·4963
0·09951		T^- 0·5021	− 0·0007	0·4979
0·1493		T^- 0·5008	+ 0·00003	0·4996
AgNO$_3$ 40°.				
0·04989	LiCl Ag	T^+ 0·47305	− 0·00007	0·4729
0·0914		T^+ 0·47396	− 0·00025	0·4737
0·1493		T^+ 0·4744	− 0·00048	0·4739
ZnBr$_2$ 40°.				
0·009933	Di-methyl aniline azo benzyl trimethylammonium nitrate. Mercury.	T^+ 0·4070	+ 0·0006	0·4076
0·03836	Zn Acetate Ag	T^- 0·5932	− 0·0001	0·4069
0·05722		T^- 0·5973	− 0·0002	0·4029
0·08787		T^- 0·6082	− 0·0003	0·3921
0·1468		T^- 0·6215	− 0·0004	0·3789
HCl 50°.				
0·04965	LiCl Ag-AgCl	T^+ 0·8073	+ 0·00024	0·8075
0·09945		T^+ 0·8106	+ 0·00048	0·8111
0·1490		T^+ 0·8125	+ 0·00074	0·8133

at 25° (0·4906) the value at 50° (0·4917) has been calculated. For this extrapolation KCl was chosen on account of the very small change of transport number with concentration.

By using the data for KCl obtained in this manner in conjunction with the infinite dilution equivalent conductivity data given in the Tables I. and II. for the other salts, the infinite dilution mobilities in Table III. and the transport numbers in Table I. were obtained.

The values of $T_+°$ at 40° shown in Table I. were obtained by intrapolation of the 50° values and Longsworth's data for the same salt at 25°.

Discussion of Results.

The H^+ ion transport number curve for HCl at 50° approaches the limiting slope in the same manner as in the 25° data of Longsworth.[1]

The Ag^+ curve at 40° approaches the $T_+°$ value in the abnormal manner common to nitrates, although the curve at 40° deviates less from the calculated slope than does that of the same salt at 25°.

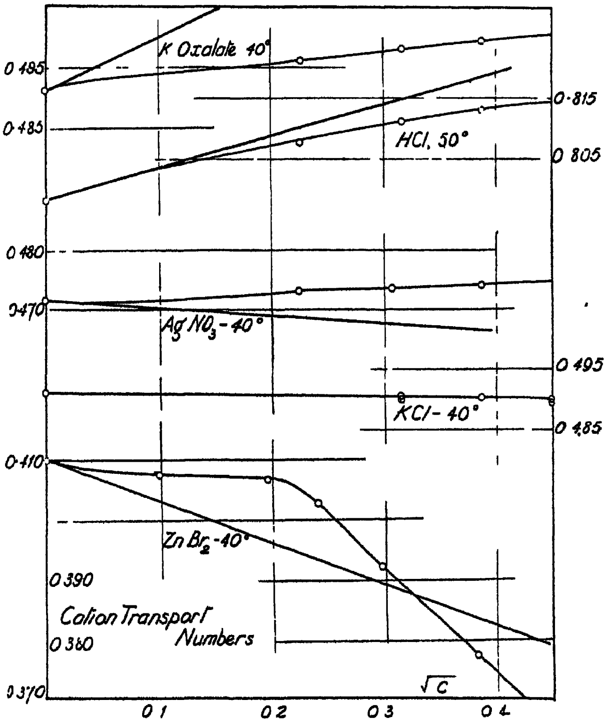

FIG. 1.

The $ZnBr_2$ curve approaches the limiting slope with a reasonable deviation for a uni-bi-valent electrolyte, but, as the concentration increases, the deviation is found to reach a maximum and then to fall off steeply, intersecting the limiting slope at 0·11 *N*. The p_H values of the solutions of $ZnBr_2$ showed that hydrolysis alone could not account for this abnormal behaviour of the Zn^{++} ion. Since ZnI_2, CdI_2 and $CdBr_2$ at higher concentrations all have anion transport numbers greater than 1, our results in the case of $ZnBr_2$ are not surprising, and may be due to the formation of a complexion of the type $Zn(Br_4)^{=}$. The potassium oxalate data do not agree with the generalisation that the slower ion has the higher temperature coefficient. The K oxalate curve appears to be normal and approaches the limiting slope in the usual manner for uni-di-valent electrolytes.

Summary.

Measurements of the transport numbers of aqueous solutions of KCl, $AgNo_3$, $ZnBr_2$ and potassium oxalate at 40° and HCl at 50° have been made by the moving boundary method. The transport number at infinite dilution for the K ion in KCl at 40° has been determined, and is 0·4913 ± 0·0003. The mobilities of a number of ions at 50° and the infinite dilution transport numbers for the above-mentioned salts have been calculated.

The author would like to thank Mr. G. S. Hartley for the valuable advice and criticism he has given through this research, and the Department of Scientific and Industrial Research for a grant.

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London.

VISUAL BALANCE-DETECTORS FOR CONDUCTANCE BRIDGES.

By C. Morton.

Received 22nd December, 1936.

It is probably due partly to the lack of a convenient and sensitive balance-detector that conductometric methods of analysis have not been widely adopted. A visual indication is preferable to an aural one, and it is desirable that the null-point detector should possess directional characteristics, *i.e.*, the direction of the deflection should indicate the sense of the adjustment necessary to attain balance. Unfortunately the electrodynamometer — the only type of A.C. galvanometer which satisfies this condition — has the drawbacks that in general a false zero is obtained, and that a reflecting movement is necessary in order to obtain adequate sensitivity. The devices now described are the outcome of attempts to design a visual balance-detector possessing the directional characteristic of the electrodynamometer, but free from these disadvantages.

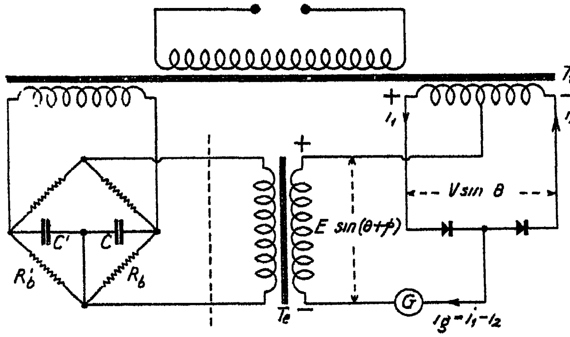

FIG. 1.—Metal Rectifier Balance-Detector (half-wave).

Metal Rectifier Balance-Detector (Half-Wave Type).

The circuit of the device is shown in its simplest form to the right of the vertical broken line in Fig. 1. An auxiliary E.M.F. of amplitude *V* (about 1 volt) is applied, by means of a transformer T_v having a centre-tapped secondary winding, to two series-connected half-wave rectifier elements. The latter may conveniently consist of two adjacent elements of a Westinghouse " bridge rectifier " of the non-reactive type. The detector terminals of the bridge are joined to the primary winding of the transformer T_e, the secondary winding of which is connected to the centre-tap of the transformer T_v and also through a direct-current galvanometer G to the junction of the two rectifier elements. If now adjustment of the bridge be made continuously in the direction required to attain balance, it is found that the galvanometer deflection decreases, passes through zero at the balance-point, and changes sign.

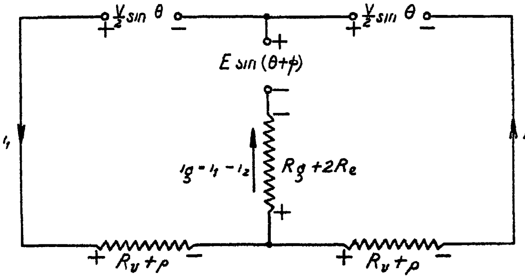

FIG. 1*a*.—Equivalent electrical circuit of Figure 1.

Let R_g, ρ, R_e, R_v be the resistances of the galvanometer, of each rectifier element, and of half-secondaries of the transformers T_e and T_v respectively. The instantaneous values of the auxiliary E.M.F., and of the E.M.F. to be detected, are $V \sin \theta$ and $E \sin (\theta + \phi)$ respectively, where $\theta = 2\pi ft$ and ϕ is the angle of phase difference between E and V. Fig. 1*a* represents the equivalent electrical network. Applying Kirchhoff's laws to the two meshes, we obtain

$$\frac{V}{2} \sin \theta + E \sin (\theta + \phi) = i_1(R_v + \rho) + (i_1 - i_2)\,(R_g + 2R_e)$$

and $$\frac{V}{2} \sin \theta - E \sin (\theta + \phi) = i_2(R_v + \rho) - (i_1 - i_2)(R_g + 2R_e).$$

The instantaneous galvanometer current is therefore

$$i_g = i_1 - i_2 = \frac{2E \sin (\theta + \phi)}{(R_v + \rho) + 2(R_g + 2R_e)}.$$

During the succeeding half-cycle a leakage current

$$i_g^1 = 2E \sin (\theta + \phi)/[(R_v + \rho') + 2(R_g + 2R_e)]$$

flows through the galvanometer in the reverse direction, ρ' being the leakage resistance of each rectifier. Hence the mean value of the galvanometer current throughout the cycle is

$$I_g = \frac{1}{2\pi}\Big[\frac{2E}{R_v + \rho + 2R_g + 4R_e}\int_0^\pi \sin (\theta + \phi)d\theta$$
$$- \frac{2E}{R_v + \rho' + 2R_g + 4R_e}\int_0^\pi \sin (\theta + \phi)d\theta\Big]$$
$$= \frac{2E \cos \phi}{\pi}\Big[\frac{1}{R + \rho} - \frac{1}{R + \rho'}\Big],$$

where $R = R_v + 2R_g + 4R_e$.

Provided that the circuit constants be suitably chosen,

$$(R + \rho') \gg (R + \rho)$$

and $$I_g = \frac{1}{R + \rho} \cdot \frac{2E}{\pi} \cos \phi. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Evidently reversal of E with respect to V will reverse the galvanometer current : in other words, the instrument has the desired directional characteristic. Provided that the resistances of the rectifiers be equal, fluctuations of the auxiliary E.M.F. have no disturbing influence on the galvanometer zero, the changes in i_1 and i_2 being equal. Fortunately, when carrying equal currents, the resistances of adjacent elements of a Westinghouse bridge rectifier rarely differ by more than 1 to 2 per cent. The factor $1/(R + \rho)$ in equation (1) is the differential conductance of the instrument. In order to obtain high conductance, the rectifier should have the maximum cross-sectional area and current-carrying capacity consistent with the requirement that it must be non-reactive at the frequency employed: for similar reasons, the galvanometer and transformers should be of low ohmic resistance.

In the preceding description it has been assumed that the secondary winding of the transformer T_v is accurately tapped at its electrical centre. In order to ensure symmetry, the centre-tapped winding may with advantage be replaced by a split secondary, the two halves of which are connected by a potential divider having a resistance of a few ohms; the sliding contact of the potential divider is connected to the secondary of the transformer T_e, and is adjusted so that the galvanometer is undeflected when $E = 0$. The amplitude of the auxiliary voltage V should be such as to ensure a favourable ratio ρ'/ρ. In practice, no substantial gain in sensitivity results from employing an auxiliary E.M.F. in excess of 1 volt, and any considerable increase over this value is liable to cause injury to the rectifiers.

Metal Rectifier Balance-Detector (Full-Wave Type).

The simple arrangement described above has the disadvantage that mechanical resonance of the galvanometer movement may occur at certain frequencies, due to the fact that the current is intermittent. The difficulty may be overcome by employing the full-wave circuit of Fig. 2. It should be pointed out that the rectifying elements are assembled in a manner which differs from that adopted in the well-known "bridge rectifier." During the instantaneous conditions represented in the figure, a relatively large current

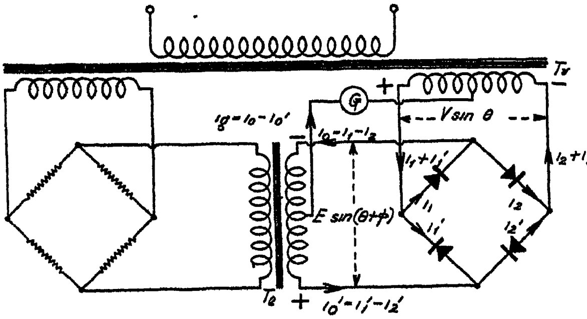

FIG. 2.—Metal Rectifier Balance-Detector (full-wave).

$$i_0 = i_1 - i_2 = \frac{E \sin (\theta + \phi)}{R_v + 2R_e + 2R_g + \rho}$$

flows *via* the upper pair of rectifiers: simultaneously, the lower rectifiers pass a small leakage current

$$i_0^1 = I_1^1 - i_2^1 = \frac{E \sin (\theta + \phi)}{R_v + 2R_e + 2R_g + \rho'}.$$

The resultant instantaneous galvanometer current is

$$i_g = i_0 - i_0^1 = E \sin (\theta + \phi)\left[\frac{1}{R_0 + \rho} - \frac{1}{R_0 + \rho'}\right],$$

where

$$R_0 = R_v + 2R_t + 2R_g.$$

During the next half-cycle these conditions are reversed, forward and leakage current being carried by the lower and upper rectifiers respectively : the resultant galvanometer current, however, is unchanged in direction and magnitude. The mean value of the galvanometer current throughout the cycle is thus

$$I_g = \frac{E}{\pi}\left[\frac{1}{R_0 + \rho} - \frac{1}{R_0 + \rho'}\right]\int_0^\pi \sin(\theta + \phi)d\theta$$

$$= \frac{2E\cos\phi}{\pi}\left[\frac{1}{R_0 + \rho} - \frac{1}{R_0 + \rho'}\right]$$

or $$I_g = \frac{1}{R_0 + \rho}\cdot\frac{2E}{\pi}\cos\phi \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

provided that $(R_0 + \rho') \gg (R_0 + \rho)$.

The full-wave circuit has the advantage over the half-wave arrangement that (*a*) sensitivity is increased, due to the increase in the differential conductance, (*b*) wave-form distortion is avoided, the loads imposed upon the sources of E.M.F. during successive half-cycles being equal, (*c*) external electromagnetic fields are reduced in intensity in consequence of the symmetrical character of the circuit, (d) as explained above, mechanical vibration of the galvanometer pointer is obviated.

Thermionic Balance-Detector.

Recently Cosens[1] has described a thermionic valve device which, when used as a balance-detector in an alternating-current bridge network, exhibits the directional characteristic of the electrodynamometer: unfortunately, as an auxiliary E.M.F. (of the same frequency as that applied to the bridge) of about 100 volts is required, the range of application is virtually restricted to measurements at supply frequencies. The circuit used by Cosens may be modified, as shown in Fig. 3, in such a manner as to adapt it for use at the higher frequencies employed in conductance measurements. The valves V_1V_2 are tetrodes of the type in which the inner grid functions as a space-charge grid and the outer one as the normal control grid, *e.g.*, the Cossor 210 D.G. (battery type) or 41 M.D.G. (indirectly-heated type). A steady voltage V_0 is supplied to the anodes by means of a battery or " high tension eliminator," and antiphased polarising potentials are applied to the space-charge grids. Due to the proximity of the inner grid to the cathode, an auxiliary E.M.F. of 1-4 volts suffices to reduce the anode current to zero during the half-cycles when the former electrode becomes negative, provided that the potential V_0 does not exceed the maximum value prescribed by the valve manufacturer. Let $\mu_1 = \partial v_a/\partial v_{g1}$, $\mu_2 = \partial v_a/\partial v_{g2}$, and $\rho = \partial v_a/\partial i_a$, where i_a, v_a, v_{g1} v_{g2} are the instantaneous anode current, anode potential, inner grid potential,

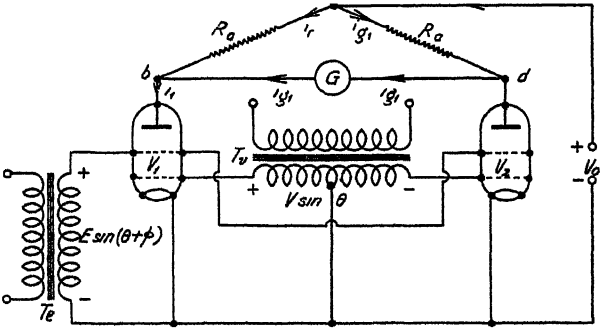

FIG. 3 —Thermionic Balance-Detector.

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[1] Cosens, *Proc. Physic. Soc.*, 1934, 46, 818.

and outer grid potential respectively. During the instantaneous conditions represented in Fig. 3 the valve V_2 is inoperative, but a current

$$i_1 = \frac{V_0 + \mu_2 E \sin(\theta + \phi) + \frac{1}{2}\mu_1 V \sin\theta}{\rho + R_a(R_a + R_g)/(2R_a + R_g)}$$

flows through the valve V_1. Using the notation of the figure, we have also $i_1 = i_r + i_{g_1}$ and $i_r/i_{g_1} = (R_a + R_g)/R_a$, whence

$$i_{g_1} = \frac{R_a[V_0 + \mu_2 E \sin(\theta + \phi) + \frac{1}{2}\mu_1 V \sin\theta]}{\rho(2R_a + R_g) + R_a(R_a + R_g)}.$$

The average value of the galvanometer current during the half-cycle is

$$I_{g_1} = \frac{R_a}{\rho(2R_a + R_g) + R_a(R_a + R_g)} \times \frac{1}{\pi}\int_0^\pi [V_0 + \mu_2 E \sin(\theta + \phi) + \mu_1 \cdot \frac{V}{2}\sin\theta]d\theta,$$

and the direction of flow through the galvanometer is from *d* to *b*. During the succeeding half-cycle V_1 passes no current, but a current

$$i_2 = \frac{V_0 - \mu_2 E \sin(\theta + \phi) + \frac{1}{2}\mu_1 V \sin\theta}{\rho + R_a(R_a + R_g)/(2R_a + R_g)}$$

flows through the valve V_2. The average value of the current flowing through the galvanometer from *b* to *d* is

$$I_{g_2} = \frac{R_a}{\rho(2R_a + R_g) + R_a(R_a + R_g)} \times \frac{1}{\pi}\int_0^\pi [V_0 - \mu_2 E \sin(\theta + \phi) + \mu_1 \cdot \frac{V}{2}\sin\theta]d\theta,$$

during the second half-cycle, and the mean galvanometer current throughout the cycle is therefore

$$I_g = \frac{I_{g_1} - I_{g_2}}{2} = \frac{R_a}{\rho(2R_a + R_g) + R_a(R_a + R_g)} \cdot \frac{1}{2\pi}\int_0^\pi 2\mu_2 E \sin(\theta + \phi)d\theta$$

$$= \frac{R_a}{\rho(2R_a + R_g) + R_a(R_a + R_g)} \cdot \frac{2\mu_2}{\pi} E \cos\phi \quad . \quad . \quad (3)$$

Maximum sensitivity is obtained when $R_a = \sqrt{\rho R_g}$, the corresponding galvanometer current being

$$I_g = \frac{1}{2\rho + R_g + 2\sqrt{\rho R_g}} \cdot \frac{2\mu_2}{\pi} E \cos\phi.$$

Sensitivity and Accuracy.

For the majority of alternating current detectors, *e.g.*, diode or triode valves or metal rectifiers operating as conventional half- or full-wave rectifiers on small E.M.F.'s, the expression connecting the mean galvanometer current I_g with the applied peak voltage E is of the form $I_g = I_0 + kE^2/(R + \rho)$, where ρ and R are the resistances of the rectifier and its associated components respectively, I_0 and k being constants.* Although Teegan,[2] Strobel[3] and others have used detectors of this type as null-point indicators in A.C. bridges, they are unsuitable for the purpose, inasmuch as the sensitivity $dI_g/dE = 2kE/(R + \rho)$ falls rapidly to zero as the balance-point is approached. On the other hand, the sensitivity $dI_g/dE = 2/\pi(R + \rho)$ of a metal rectifier balance-detector of the directional type now described is constant and independent of the applied voltage E.† A combination of a 10 mA. non-reactive Westinghouse rectifier with a 500 ohm Unipivot galvanometer, when used in the circuit of Fig. 2, gave a constant sensitivity of 0·8 microampère per millivolt (R.M.S.); with a 50 mA. rectifier and 50Ω galvanometer the corresponding value was $7{\cdot}3\mu$ A./mV., and by further reduction of the circuit resistance still higher values were obtained.

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* For the metal rectifier, of course, $I_0 = 0$.

[2] Teegan, *Phil. Mag.*, 1931, 11, 1250.

[3] Strobel, *Rev. Sci. Instr.*, 1935, 6, 319.

In the approximate analysis of the circuits it has been assumed that the bridge and detector are supplied with alternating voltages of sinusoidal wave-form, and it is clear that the presence of reactance in the bridge will introduce errors due to the harmonic content of the source. Further, as zero deflection is obtained when the component of E which is in phase with V is zero, an inaccurate reading is obtained when an angle of phase difference exists between E and V. Although an electrolytic solution normally behaves as a pure resistance when carrying alternating current, it is well known that under certain conditions it may exhibit the properties of a resistance in parallel with a condenser, as indicated by R_b and C in Fig. 1. When an apparent balance has been obtained by adjustment of $R_b{}^1$, it is advisable to reverse the leads to the detector, and a reversing switch may with advantage be incorporated in the circuit for this purpose. If a deflection is obtained, indicating the presence of reactance in the bridge, a variable air-dielectric condenser C^1 is connected across $R_b{}^1$, and adjustments of reactance and resistance are made until it is found that the galvanometer pointer is undisturbed by movements of the reversing switch. The value of $R_b{}^1$ then gives the true ohmic resistance of the electrolytic cell. Provided that precautions be taken to avoid polarisation of the electrodes, this adjustment is rarely required, and accuracy within the limits required in conductometric analysis, *viz.*: ± 0·1 per cent., is readily obtained.

Metal-rectifier balance-detectors of the directional type are obtainable commercially from the Cambridge Instrument Co., Ltd.

Summary.

A metal rectifier may be connected to a D.C. galvanometer in such a manner as to constitute a pointer A.C. balance-detector with the directional characteristic of the electrodynamometer: when used as a visual null-point detector in a conductance bridge, the direction of the deflection indicates the sense of the adjustment necessary to secure balance. The instrument has a wide frequency range, and is capable of detecting an alternating potential of 0·1 millivolt. A thermionic A.C. balance-detector with similar directional characteristics is also described.

A grant from the Dixon Fund of the University of London is gratefully acknowledged.

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S.W. 3.

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† It is here assumed that E and V are in phase.

THE REACTIONS OF SCANDIUM AT THE DROPPING MERCURY CATHODE.

By R. H. Leach and H. Terrey.

Received 15*th January*, 1937.

Though scandium is usually regarded as a rare earth, it closely resembles aluminium, the adjacent member of the third group of the Periodic Table. It has been shown that aluminium can be determined at the dropping mercury cathode under the conditions used in the polarograph.[1] The object of this work has been to examine whether scandium can be detected at the dropping mercury cathode, and whether its reactions at this electrode can be used for qualitative and quantitative estimation of the element. At present scandium is determined quantitatively by formation of the oxide. This is difficult when small quantities have to be estimated, and the polarographic method offers a rapid and sensitive means of analysis.

Experimental.

The investigations of the reactions of scandium at the dropping mercury cathode have been carried out with the polarograph made by Messrs. Leybold's Nachfolger A-G. The design of this instrument closely follows that described by Heyrovsky,[2] and will not be given here.

The current-voltage curves were automatically recorded on a drum camera, loaded with bromide paper printed with millimetre squares. The rotating potentiometer of the polarograph was wound with twenty turns of wire, and each complete rotation was recorded on the film by a flash of light. The vertical lines so obtained served to calibrate the film. The galvanometer used had a maximum sensitivity of $2{\cdot}6 \times 10^{-9}$ amps. mm./m. Its period of oscillation was about three seconds. By means of an Ayrton variable shunt the sensitivity of the galvanometer could be adjusted between 1 (maximum) and 1/10,000th (minimum).

The design of the dropping mercury cathode itself has been slightly modified. Heyrovsky and his workers have used a capillary jet attached to a long piece of rubber tubing with a glass reservoir at the top. The rate of flow of mercury was then adjusted by altering the height of the reservoir. We have found this troublesome, and have preferred to replace the rubber tubing by a long hard glass tube tapered at the lower end. The pyrex capillary jet was attached to the tapered end by a short piece of rubber pressure tubing, so that the two glass surfaces were in contact. The rate of flow of mercury through the jet was adjusted by varying the height of liquid in the tube. For this purpose the tube was fitted with a side tap. Electrical contact to the cathode was made by a platinum wire fused into the side of the tube at the lower end. In this way we were able to obtain a steady flow of mercury, whose rate of flow could be readily adjusted.

The capillary jets were drawn out from pyrex capillary tubing of one to two millimetres bore. The sizes of the jets were such that from a column of mercury 60 centimetres high, the rate of flow of mercury was one drop in six or seven seconds, when the jet was under distilled water.

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[1] J. Prajzler, *Coll. Trav. chim. Tchec.*, 1931, 3, 410.

[2] J. Heyrovsky, and M. Shikata, *Rec. Trav. chim. Pays-Bas*, 1925, 44, 496.

The electrolytic cells used were types 2 and 3 illustrated by Heyrovsky.[3] The cells had a maximum capacity of 15 millilitres, and usually about 10 millilitres of solution were used. The cells were cleaned with concentrated nitric acid, and well washed with distilled water.

The following experimental procedure was used. The solution to be examined was placed in the cell over a layer of mercury, which served as the anode. Contact to the anode was made by a platinum wire fused through the side of the vessel. Hydrogen was bubbled through the solution for forty to fifty minutes. This was found to be sufficient time to suppress the oxygen waves on the polarographic curves.[4]

Before recording the curves, the potential of the mercury anode relative to the normal calomel electrode was measured. The electrolytic cell was connected to a saturated solution of potassium chloride into which the normal calomel element dipped. The bridge from the cell to the potassium chloride solution was a capillary tube fitted with a tap. This was filled with solution in the cell. The use of an agar-agar bridge was avoided to prevent the presence of reducible organic impurities, which would appear on the polarographic curves. The potential of the system was measured on a potentiometer.

The bridge was removed from the cell and replaced by the dropping cathode, whose rate of flow in the solution was one drop in three or four seconds, and the polarographic curves were photographed.

When all the curves had been recorded, the total potential applied to the drum, about four volts, was measured with a potentiometer as the instrument was not fitted with a compensating element.

Throughout the work solutions of scandium chloride and alkali and alkaline earth chlorides were used. The solutions of scandium chloride were prepared from pure anhydrous scandium chloride, $ScCl_3$. The latter was made by the method of Smith.[5] Pure scandia, Sc_2O_3 (prepared by Sir W. Crookes) was heated in a quartz tube to 750° C. in a mixture of carbon tetrachloride vapour and argon. The chloride volatilised off as white crystals, which were dissolved in distilled water. The solution was slightly acid owing to hydrolysis of the chloride. Solutions of potassium chloride, lithium chloride, ammonium chloride and barium chloride were prepared by dissolving the A.R. compounds in distilled water. They were examined polarographically to ensure that there were no detectable impurities. A pure solution of hydrochloric acid was prepared by distillation.

The following procedure was used for the determination of the " half-wave " potentials of the curves. From each solution a series of curves was obtained on one plate. These curves differed only in the sensitivity of the galvanometer, the concentration of the solution and the total applied voltage being unaltered. Care was taken that all the curves started from the same zero point of the abscissa. This is illustrated in Fig. 1. The mid-point of each wave was then measured, and a vertical line drawn to represent the mean of these points. The value of the voltage where this line cut the abscissa was taken as the mean half-wave potential; the value was then calculated with reference to the normal calomel electrode.

To obtain the mid-point of a wave, the following geometrical construction was employed. Parallel tangents were drawn one at the lower bend of the curve and one at the upper bend. A parallel tangent was drawn through a point midway between the two tangents, and the point where the third tangent cut the wave was taken as the mid-point.

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[3] *Physikalische Methoden der Analytischen Chemie*, vol. 2, Böttger (Akad. Verlagsg., 1936), p. 277, Fig. 11.

[4] Böttger,[3] pp. 279, 307.

[5] N. H. Smith, *J. Amer. Chem. Soc.*, 1927, **49**, 1645.

Discussion of Results.

The curves shown in Fig. 1 were obtained from an *N*/50 solution of scandium chloride and *N*/10 potassium chloride, the sensitivity of the galvanometer being varied from 1/50th in the top curve to 1/1000th in the bottom curve. Like aluminium, scandium gives rise to waves when reduced at the dropping mercury cathode. It can be seen that oxygen is just detectable on the most sensitive curve.

The scandium waves are similar to those given by aluminium. They are not symmetrical, the curvature at the bases of the curves being very shallow. With aluminium, it has been shown that this shallow curvature is due to hydrogen ;[6] the rest of the wave is, however, too sharp for hydrogen, being typical of a trivalent ion. As previously stated, solutions of scandium chloride are acid owing to hydrolysis. It is therefore likely that the curves, like those of aluminium, are due to the simultaneous deposition of hydrogen and scandium. To show that this is so, curves were recorded of a solution of scandium chloride to which hydrochloric acid was added. The results are shown in Fig. 2. Curve 1 was obtained from an *N*/50 solution of scandium chloride in *N*/10 potassium chloride; the sensitivity of the galvanometer was 1/500th. Curve 2 was obtained from the same solution, when 1/10th millilitre of *N*/6 hydrochloric acid was added, the sensitivity of the galvanometer being unaltered. The subsequent curves were obtained by further increasing the concentration of hydrochloric acid, 1/10th millilitre at a time.

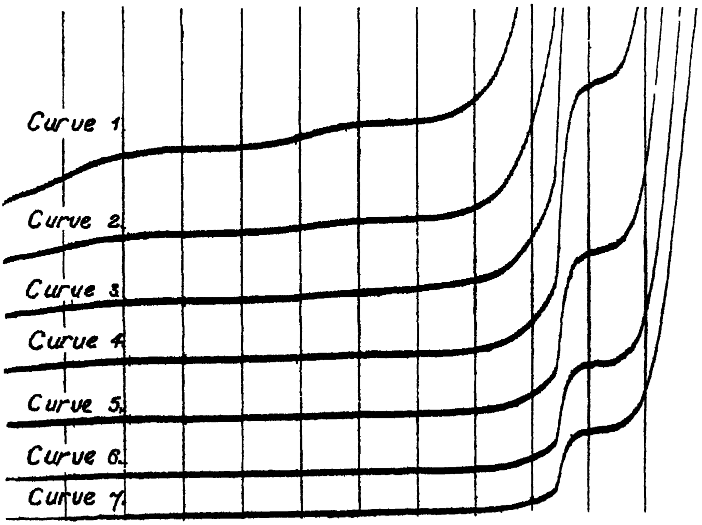

FIG. 1.—Curves of an N/50 solution of scandium chloride in N/10 potassium chloride. The sensitivity of the galvanometer changes from 1'50 in curve 1 to 1/1000 in curve 7.

As the concentration of hydrochloric acid is increased, the single curve is gradually broken up into two curves, the first being due to the deposition of hydrogen, and the second due to the deposition of scandium. It can be seen that the base of the scandium wave is much sharper than that of the hydrogen wave. The scandium wave has become symmetrical, and has a steeper slope than that due to hydrogen. As the concentration of hydrochloric acid is increased, the position of the scandium wave becomes more negative to a limiting value, as shown in curves 5 and 6 of Fig. 2.

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[6] J. Prajzler, *Coll. Trav. chim. Tchec.*, 1931, 3, 411.

In curves 3, 4, 5 and 6 the height of the scandium wave has reached a constant value, showing that separation from hydrogen is complete.

It has been found that the mean value for the deposition potential of scandium referred to the normal calomel electrode is − 1·84 ± 0·01 volts.

An examination of the deposition potentials of the elements shows, as a general rule, that the value becomes more positive with increasing atomic number for a given group of the Periodic Table.* The values for Group 1 are anomolous, but the potentials are very close together. Group 2 obeys the rule (magnesium gives no wave on the polarograph); and Group 3 shows no anomoly until scandium is introduced, which has a more negative deposition potential than aluminium, in spite of its higher atomic number. (The value for the deposition potential of aluminium is given by Heyrovsky as − 1·79 volts.) Preliminary experiments with yttrium indicate that its deposition potential is more positive than aluminium, which is in accordance with its higher atomic number. The deposition potentials of scandium and yttrium, if fairly widely separated as expected, will offer a valuable method of following the separation of these two very similar elements.

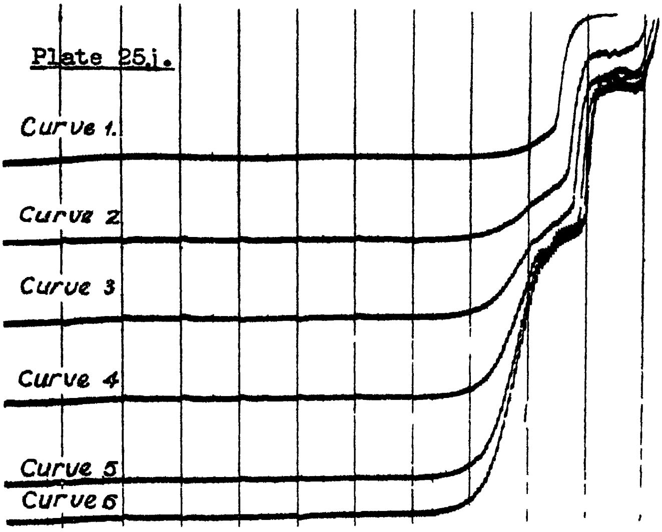

FIG. 2.—Addition of hydrochloric acid to a solution of scandium chloride. Sensitivity of galvanometer 1/500.

The deposition potentials of scandium and aluminium differ only by 0·05 volts. The width of a trivalent wave is of the order of 0·15 volts. It was therefore thought doubtful that the two elements could be completely separated when present together in solution. This was investigated by treating a solution of scandium chloride in lithium chloride with a solution of aluminium chloride. The results are shown in Fig. 3. Curve 1 was obtained from 12 millilitres of an *N*/50 solution of scandium chloride in *N*/5 lithium chloride, the solution being sufficiently acid to separate scandium and hydrogen. The sensitivity of the galvanometer was 1/500th, and remained unaltered during the subsequent curves. Curve 2 was obtained on adding 0·1 ml. *N*/2 aluminium chloride solution to the solution of curve 1, and curves 3 and 4 on adding 0·2 and 0·5 ml. of aluminium chloride respectively.

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* A table of the latest accepted values for Deposition Potentials is given in Böttger,[8] pp. 294 and 295.

Addition of aluminium chloride to a solution of scandium chloride causes the scandium wave to break up into two parts, but in no case can two completely separate waves be obtained. If the heights of each portion of the wave are measured, the values obtained are those shown in the table below.

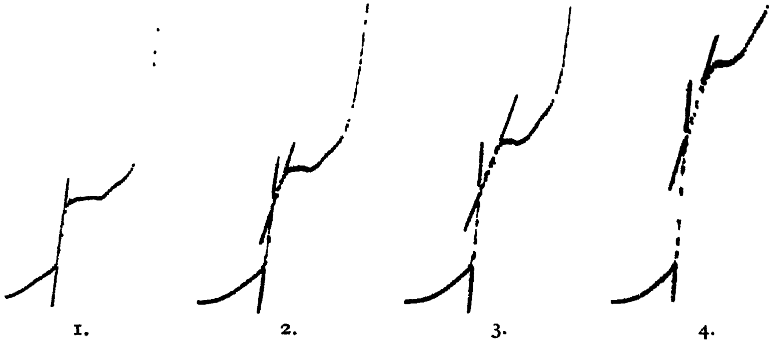

Fig. 3.—Addition of aluminium chloride to a solution of scandium chloride (see text).
The separation has been indicated by continuing each part of the waves.

The height of the scandium wave varies considerably, although the concentration of the scandium remains virtually constant. The ratio of the heights of the aluminium waves is approximately 1 : 1·2 : 1·8; whereas the ratios of the concentrations of aluminium are nearly 1 : 2 : 5. It is evident that no quantitative measurements of concentration or even relative concentration can be made when aluminium and scandium are present together. They can, however, be detected simultaneously when they are of the same order of concentration.

Curve.	1.	2.	3.	4.
	mm.	mm.	mm.	mm.
Sc wave .	18·0	9·0	13·5	18·0
Al wave .	0·0	17·0	20·0	31·0

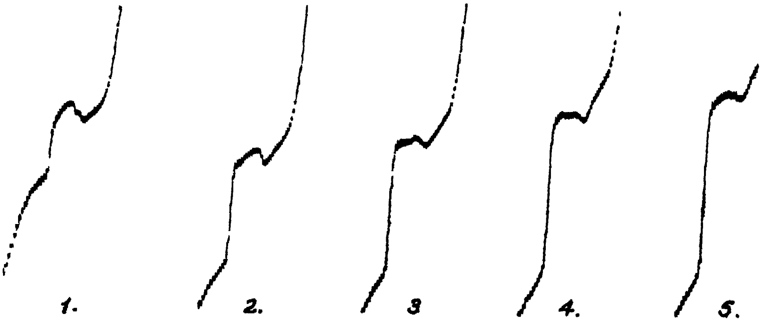

Fig. 4.—Curves showing the change in height of waves from scandium chloride solutions with change of concentration. Sensitivity of galvanometer 1/500th.

To show the scandium alone can be quantitatively estimated with the polarograph, the method of Hohne [7] has been adopted. To 10 ml. of a base solution such as lithium chloride, 1 ml. of scandium chloride was added. The curve obtained from this solution is shown in curve 1, Fig. 4. Another millilitre of the scandium chloride solution was then added, and the polarogram recorded, curve 2. This was repeated four times, to give the series of curves illustrated. The height of each wave was then measured, and the relative concentrations calculated, in this case 1/11, 2/12, 3/13, 4/14 and 5/15. A graph was plotted of the heights of the waves against the relative concentrations of scandium in the solutions. Graph I. of Fig. 5 was obtained from the curves of Fig. 4. The graph was a straight line, showing that the height of the scandium wave is a linear function of the concentration of scandium in the solution. To use this fact to determine the concentration of an unknown solution, a graph of this type would be obtained by the above procedure with a solution of scandium chloride of known strength. At the same time, a curve of the unknown solution would be recorded, using the same jet and cathode. From the height of the wave the concentration could then be obtained from the curve. It is important that the solution is made sufficiently acid to separate the scandium from hydrogen, or the linear relation does not hold. Graph II. of Fig. 5 was obtained from curves of a solution which contained insufficient acid.

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[7] Private communication from Dr. Hohne.

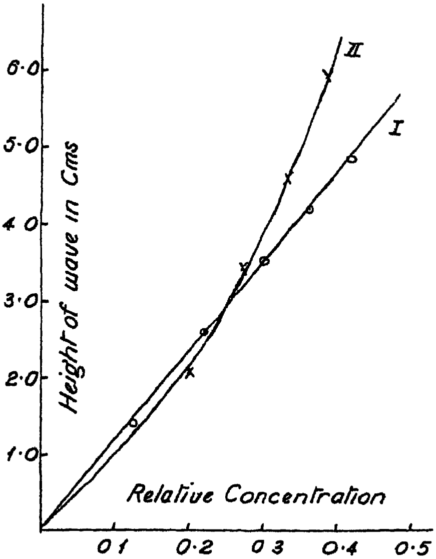

FIG. 5.—Graph I. illustrates the linear relationship between height of scandium waves and concentration.
Graph II. is obtained from a solution containing insufficient acid.

Conditions for the Detection of Scandium.

It has been shown above that scandium can only be detected quantitatively when the solution is acid.

The definition of the scandium wave depends on the nature and concentration of the base electrolyte. Well defined waves are obtained with barium and potassium chloride solutions, provided the concentration is not greater than $N/10$. In more concentrated solutions the top of the scandium wave does not become horizontal. This naturally follows as the turning point of the potassium and barium deposition becomes more positive with increasing concentration. Ammonium chloride is not satisfactory, the top of the scandium wave always being very badly defined. Lithium chloride is the best base electrolyte owing to its very negative deposition potential. With this electrolyte and a galvanometer sensitivity of 1/500th, $N/50$ scandium chloride solutions give waves 2 centimetres high. Since it is possible to work to a sensitivity of 1/10th with the galvanometer, concentrations of scandium as low as 10^{-4} normal can be accurately estimated. Concentrations as low as 10^{-5} normal can be detected, but the shape of the wave is too uncertain for an accurate determination of the concentration.

Summary.

The determination of the deposition potential of scandium at the dropping mercury cathode is described with experimental detail. The value of the deposition potential is given as — 1·84 ± 0·01 volts, relative to the normal calomel electrode.

It is shown that the polarographic method can be used for the qualitative and quantitative estimation of scandium. The conditions of the solutions and the limitations of the method are described, with particular reference to the simultaneous estimation of scandium and aluminium.

A modified form of dropping mercury cathode is described.

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KINETICS OF CO-ORDINATION REACTIONS IN THE COBALTAMMINE SERIES. I. THE AQUOTISATION OF THE CHLOROPENTAMMINE ION.

By F. J. Garrick.

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1. Introductory.

Complex ions of the cobaltammine and similar groups are in general capable of undergoing a number of slow reactions in solution whereby a group (acid radicle or neutral molecule) is eliminated from the co-ordination sphere and replaced by another from the surrounding medium. In view of their importance it is rather surprising that so few of these reactions have been studied in detail. A knowledge of their rates, and hence of the corresponding equilibria,[1] would be of interest not only for the systematic chemistry of the group, but also as throwing some light on the nature and stability of the linkages concerned. Moreover these reactions are of considerable interest from the standpoint of kinetics, in that they are ionic reactions of widely varying valence types each of which is one of a group in which the reacting ions are chemically different but similar in charge, radius, and general configuration.

This paper describes a study of the aquotisation of the chloropentammine cobaltic ion, whereby the acido-chlorine is replaced by a water molecule. $[Co5NH_3 . Cl]^{2+} + H_2O \rightarrow [Co5NH_3 . H_2O]^{3+} + Cl^-$. A few measurements of the rate of this reaction in its early stages were made by Lamb and Marden.[2]

The objects of the present investigation were to establish the general course of the reaction and to measure the rate and its temperature coefficient under conditions such that due allowance might be made for the effect of the reverse reaction where necessary.

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[1] Direct measurements of the equilibria are usually impracticable. See *e.g.*, Lamb and Marden, *J. Amer. Chem. Soc.*, 1911, **33**, 1882; Pers, *C.R.*, 1911 **153**, 673.

[2] *Loc. cit.*[1], p. 1873.

It was decided to follow the reaction by direct determination of the free chloride ion, since there was some doubt as to the accuracy and general applicability of the conductivity method, and this necessitated some preliminary work on the conditions under which chloride ion can be quantitatively determined in presence of the chloropentammine ion. Experiment showed that dilute silver nitrate causes the acido-chlorine to be eliminated (as silver chloride) much more rapidly than by the aquotisation reaction, but indicated that the effect of this could be rendered negligible under suitable conditions. The method of analysis which was evolved was tested on freshly prepared solutions of chloropentammine chloride, and this led to some investigation of methods of purifying this substance.[3] When a pure specimen of the salt had been obtained the method was found to be accurate.

In future investigations it is hoped to make a detailed study of the reverse reaction and of the reaction with silver ions which has been alluded to.

2. Experimental.

Materials.

The cobaltammine salts used were aquopentammine chloride, chloropentammine chloride, nitrate and perchlorate, and hexammine nitrate and perchlorate.[4] Other substances used in studying salt effects were freed from chloride where necessary by recrystallisation.

The starting-point for pure roseo- and chloro-purpureo-salts was roseo-oxalate, which had been prepared by the method of Jörgensen,[5] and freed from luteo-oxalate by solution in cold dilute ammonia. The residue of the latter salt was used as the source of luteo-salts.

Aquopentammine Chloride.—The oxalate was dissolved in dilute HCl and the solution cooled in ice and precipitated with concentrated HCl. The salt was purified by dissolving it in water at room temperature, and again precipitating it by cooling in ice and adding HCl.

Chloropentammine Chloride.—The method of purification has already been described.[3]

Chloropentammine Nitrate and Perchlorate.—$CpCl_2$ was washed with moderately dilute nitric or perchloric acid until free from chloride. The product was dissolved in water and reprecipitated by addition of the corresponding acid.

Hexammine Nitrate and Perchlorate.—The luteo-oxalate was washed with dilute ammonia then dissolved in dilute HCl and reprecipitated by pouring into excess ammonia so as to ensure freedom from roseo-salt. The precipitate was dissolved in the appropriate dilute acid and the required salt thrown down by adding excess of the acid. The salts were purified by reprecipitation from water by excess of the acid.

After the final precipitation, all the salts were washed successively with the dilute acid, alcohol, and ether, and after removing the last-named by evacuation or by exposure to air they were kept in a vacuum desiccator over sulphuric acid.

Particular precautions were necessary with $Cp(ClO_4)_2$ on account of its hygroscopic character. After thorough drying in vacuo over sulphuric acid, it gains about 0·5 per cent. of its weight in a minute or so on exposure to the air of the laboratory, but apparently on prolonged exposure does not take up more than about 2 per cent. of its weight of water. This may possibly indicate the existence of a hemihydrate. Ephraim[6] describes the salt as anhydrous and does not refer to its hygroscopic character. He finds a percentage of cobalt about 0·4 per cent. below the theoretical.

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[3] Garrick, *Z. anorg. Chem.*, 1935, **224**, 27.

[4] These will be denoted by abbreviated formulæ using Ro, Cp, and Lu as symbols for the roseo, chloropurpureo and luteo radicles.

[5] *Z. anorg. Chem*, 1898, **17**, 460.

TABLE I.—ANALYSIS OF MATERIALS.

Salt.	Ionisable Chloride (Per Cent.).	Total Chloride (Per Cent.).	
$CpCl_2$	28·29 28·31	42·50 42·46	Found calculated
$Cp(NO_3)_2$	none detectable 0·00	11·61 11·67	Found calculated
$Cp(ClO_4)_2$	none detectable 0·00	9·36 9·37	Found calculated
$RoCl_3$	39·64 39·62	39·68 39·62	Found calculated

The luteo-salts were tested for chloride but not otherwise analysed. The other cobaltammine salts were analysed for ionised and/or total chloride. Some typical analyses follow (Table I.). Ionisable chloride was determined by the gravimetric method used in following the reaction (see below), and total chloride either gravimetrically after bringing about complete aquotisation by warming with ammonia, or volumetrically after decomposition of the complex ion by heating with caustic alkali.

Rate Measurements.

The rate measurements were carried out in an electrically-controlled thermostat which maintained a constant temperature to within 0·01° C.

Solutions were made up to a definite volume with known weights of salt, the water (or electrolyte solution) being previously warmed to the appropriate temperature. Usually 250 c.c. of from 0·007*M* to 0·015*M* solution was used, but the volume was varied in some experiments. The results were independent of the volume over a range of from 100 c.c. to 2 litres, so that wall effects are absent. In some experiments the flasks were made opaque with black lacquer without influence on the results.

In the earlier part of the work analyses were carried out by a gravimetric method based on the work which has been referred to. The necessary working conditions included the use of a minimal excess of silver and rapid working and washing in the cold. Details have been published elsewhere.[3] When using this method, the whole of the solution was usually analysed in bulk after from two to five days at 25°, or corresponding times at other temperatures, but in some cases samples taken by pipette were analysed at intervals over much longer periods. The final time was taken as that at which the solution was immersed in ice.

The gravimetric method, though accurate, was inconvenient. It was often necessary to make a preliminary rough analysis so as to avoid using too much silver (for the time restriction made any other method impracticable), and there was always the danger of some accidental delay prolonging unduly the time during which silver ions were present, and thus causing an erratic high result. Accordingly, while rate measurements were in progress, a search was made for a more convenient method. Ultimately it was found that the chloride ion could be potentiometrically titrated with silver nitrate, using a simplified potentiometric system, sufficiently rapidly and with the desired accuracy. This method was used in most of the later work. The results of the two methods agree well. In using this method samples (usually 50 c.c.) were pipetted at suitable intervals of time. When working at higher temperatures the solution was cooled and the time taken up to cooling; in other cases the temperature remained near to that of the experiment during titration and the time was taken up to attainment of the end-point. (The temperature was noted during titration, and if necessary a slight correction could be applied, knowing the temperature coefficient of the reaction velocity. This correction never amounted to more than 0·3 per cent.

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[6] *Ber.*, 1923, 56, 1538.

Consideration of the various sources of error showed that a single determination (*i.e.* a single analysis) might give a constant in error by about 2 per cent. in the least favourable circumstances. On the mean result of a series the error should be less than 1 per cent. The concordance of the results is such as to bear out this conclusion.

3. Velocity Equations.

In describing the results the following notation will be used :—

a = initial concentration of Cl^- ion,
b = initial concentration of Cp^{2+} ion,
c = initial concentration of Ro^{3+} ion,
x = increase in concentration of Cl^- ion after time t,
$-x = y$ = decrease in concentration of Cl^- ion after time t.

For the reverse of the aquotisation reaction, *i.e.*, in this instance $Ro^{3+} + Cl^- \rightarrow Cp^{2+} + H_2O$, the term "de-aquotisation" will be employed, and the aquotisation and deaquotisation reactions will be denoted in brief by A-reaction and D-reaction respectively.

k_A = velocity constant for A-reaction,[7]
k_D = velocity constant for D-reaction,
k_A'', k_A', k_D' = various approximations to k_A and k_D.

Assuming that the A- and D-reactions are respectively pseudo-unimolecular and bimolecular, as indicated by the stoichiometric equation

$$Cp^{2+} + H_2O \rightleftharpoons Ro^{3+} + Cl^-,$$

we find for the former

$$\frac{dx}{dt} = k_A(b - x) - k_D(a + x)x, \quad . \quad . \quad . \quad \text{(i)}$$

where $a = 2b$ in $CpCl_2$ and $a = 0$ in other cases, and for the latter

$$\frac{dy}{dt} = k_D(a - y)(c - y) - k_A y, \quad . \quad . \quad . \quad \text{(ii)}$$

where in $RoCl_3$ $a = 3c$.

These equations lead to the following integrals :

from (i)
$$(P + Q) \,.\, k_D \,.\, t = \ln \frac{P(Q + x)}{Q(P - x)}, \quad . \quad . \quad . \quad \text{(iii)}$$

where
$$PQ = bk_A/k_D, \quad Q - P = a + k_A/k_D,$$

and from (ii)
$$(Q' - P') \,.\, k_D \,.\, t = \ln \frac{P'(Q' - y)}{Q'(P' - y)}, \quad . \quad . \quad . \quad \text{(iv)}$$

where
$$P'Q' = ac, \quad P' + Q' = a + c + k_A/k_D.$$

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[7] *I.e.* the pseudo unimolecular constant.

These integrals are used to calculate the course of the reaction from given values of the constants, but to determine the constants from experimental data other (approximate) integrals are more convenient.

Neglecting k_D gives as a first approximation to k_A

$$k_A'' = \frac{1}{t} \ln \frac{b}{b - x}. \quad . \quad . \quad . \quad . \quad (v)$$

A closer approximation is obtained by neglecting x^2, thus

$$k_A' = \frac{1}{\beta t} \ln \frac{b}{b - \beta x}, \quad . \quad . \quad . \quad . \quad (vi)$$

where $\beta = 1 + a \, . \, k_D/k_A$. Of course, when $a = 0$, $k_A'' \equiv k_A'$.

Finally further approximation leads to

$$k_A = \left(1 - \frac{2\alpha b}{\beta^2}\right)k'_A + \frac{\alpha}{\beta^2} \cdot \frac{x}{t} \cdot \frac{2b - \beta x}{b - \beta x}, \quad . \quad . \quad (vii)$$

where $\alpha = k_D/k_A$ and β has the same significance as before. Equations (vi) and (vii) are easily solved by successive approximation, beginning with k_A''.

Similarly for k_D, by neglecting k_A we have as a first approximation

$$k_D' = \frac{3}{2at} \ln \frac{a - y}{a - 3y}, \quad . \quad . \quad . \quad . \quad (viii)$$

and can then solve by successive approximations the more exact equation

$$k_D = \gamma \, . \, k_A \, . \, \frac{y}{ac} \cdot \frac{e^{\gamma k_A t}}{e^{\gamma k_A t} - 1}, \quad . \quad . \quad . \quad (ix)$$

where $\gamma = 1 + \alpha(a + c)$ and α has the same significance as before.

The inaccuracy of the final approximations is always less than the experimental error. In the tables of results the values of k_A'' and k_A' are given as well as the final values of k_A so as to illustrate both the nature of the approximations and the influence of reversibility.

4. Results.

In what follows, concentrations are expressed in gram-molecules per litre and times in minutes. The constants are calculated with natural logarithms. The columns headed "Method" refer to the method of analysis, "G" and "P" signifying gravimetric and potentiometric-volumetric respectively. Otherwise the tables are self-explanatory.

The relative rates of the D- and A-reactions were found to be such that the correction for the former could be reduced to 0·5 per cent. or so by determining k_A in the early stages of the reaction in a solution initially free from chloride ion.

It was, however, necessary to show that the assumptions of the last section are valid, and that the value of k_A is the same in solutions of different chloropentammine salts and is independent of the initial concentration of chloride ion.

This necessitated (*a*) determination of approximate values of k_D; (*b*) investigation of the course of the reaction over a wide range (it was for various reasons impracticable to vary the initial concentrations over more than a small range); and (*c*) comparison of values of k_A obtained in solutions of $CpCl_2$, where the effect of the D-reaction is considerable, with those obtained in other solutions where it is small.

When these points had been settled by experiments at one temperature (25·00° C.) it was possible (*d*) to determine values of k_A at a series of temperatures under such circumstances that the correction for k_D was very small, and also (*e*) to study the effect of added electrolytes on the A-reaction.

During the work it was, of course, necessary at first to proceed by successive approximations from the values of one constant to those of the other; in the tables of results the constants for each reaction have been calculated with the appropriate finally-accepted value for the constant of the opposing reaction.

(*a*) Approximate Values of k_D.

It was found that k_D depends on the ionic strength, and at ionic strengths near those prevailing in measurements of k_A the relative magnitudes of the constants, and consequently the position of the equilibrium, are such that k_D can only be rather roughly determined; the values found were subject to an experimental error of about 10 per cent. On the other hand (for the same reasons) in determining k_A the effect of k_D is small, so that an approximate value of the latter is sufficient. Thus, in the experiments with $CpCl_2$ an error of 10 per cent. in k_D produces an error of at most 0·5 per cent. in k_A, while in the experiments in which the solution was initially free from chloride ion an error of even 20 per cent. in k_D has a negligible effect on the value of k_A.

Table II. summarises values of k_D found in solutions of $RoCl_3$ with or without added electrolytes. As far as the accuracy of the work allows, these results indicate a roughly linear relationship between log k_D and $\sqrt{\mu}$, and also that the degree of acidity of the solution is without serious influence.

TABLE II.

Temp. °C.	Conc. of $RoCl_3$.	Added Electrolyte.	Conc.	Ionic Strength.	(Mean)
25·00	0·00855			0·051	4·0*
	0·02021			0·121	3·0
	0·02019	HNO_3	0·2	0·32	1·8
	0·01970	KNO_3	0·2	0·32	1·8
30·00	0·00994			0·060	8·1
	0·01440			0·085	6·0

* Mean value from de-aquotisation expt in Table III.

b) The Course of the Reaction.

Table III. gives a comparison between calculated and found values of $(a - y)$ and $(a + x)$ in experiments in which solutions of $CpCl_2$ and of $RoCl_3$ at equivalent concentrations underwent aquotisation or de-aquotisation respectively up to within 1 per cent. of the equilibrium concentration

TABLE III.

De-aquotisation.
($RoCl_3$ in water at 25·00° C.)
$a = 0{\cdot}02566,\ c = a/3 = 0{\cdot}00855.$

Aquotisation.
($CpCl_2$ in water at 25·00° C.)
$a = 0{\cdot}01710,\ b = a/2 = 0{\cdot}00855.$

t.	$(a - y)$ obs.	$(a - y)$ calc.	*t*.	$(a + x)$ obs.	$(a + x)$ calc.
1267	0·02550	0·02556	4250	0·02004	0·02002
2654	0·02546	0·02546	7185	0·02136	0·02139
5640	0·02530	0·02528	11560	0·02273	0·02274
8490	0·02514	0·02516	14470	0·02325	0·02335
12850	0·02512	0·02507	18750	0·02396	0·02393
∞	—	0·02488	28680	0·02452	0·02457
			∞	—	0·02488

of chloride ion. The calculated values are obtained with the finally-accepted value for k_A in chloride solutions and with $k_D = 4·0 \times 10^{-4}$.

These results are plotted in Fig. 1, in which the ordinates are percentage aquotisation or de-aquotisation. The curves are calculated by equations (iii) and (iv), the horizontal line is the calculated equilibrium, and the circles are experimental results.

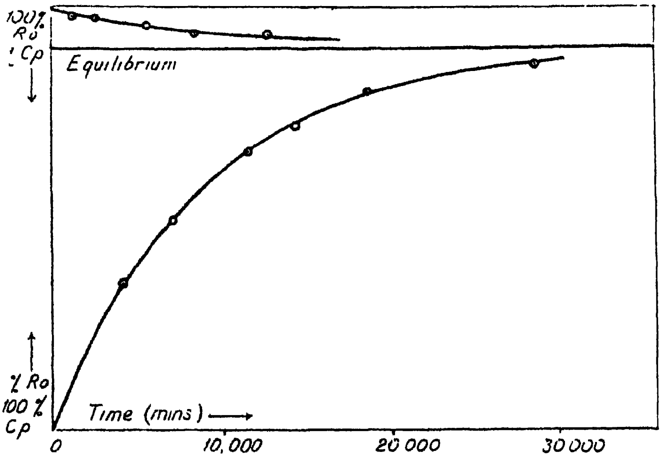

FIG. 1.

(c) Velocity of Aquotisation at 25·00° C.

As indicated in sub-section (a), it was desirable to obtain values for k_A from experiments using $CpCl_2$ as well as other salts. The ionic strengths ranged from $\mu = 0·03$ to $0·05$. From the results under (a) we find for the latter $k_D = 4·0 \times 10^{-4}$, and for the former, by a short extrapolation, $k_D = 4·6 \times 10^{-4}$. Thus the desired accuracy can be obtained by taking $k_D = 4·3 \times 10^{-4}$ in all cases. The results are shown in Tables IV., V. and VI.

TABLE IV.

$CpCl_2$ in water at 25·00° C.

$a = 2b$.	$a + x$.	x.	t.	Method.	$10^4 . k_A''$.	$10^4 k_A'$.	$10^4 k_A$.
0·01677	0·01888	0·00211	2921	G	0·995	1·007	1·008
0·02119	0·02380	0·00261	2855	G	0·986	1·004	1·005
0·02009	0·02263	0·00254	2901	G	1·000	1·019	1·021
0·01863	0·02204	0·00341	4621	G	0·987	1·008	1·011
0·01883	0·02124	0·00241	2965	P	0·997	1·004	1·005
0·01710*	0·02004	0·00293	4250	P	0·992	1·008	1·010
	0·02136	0·00426	7185	P	0·960	0·990	0·996 *
	0·02273	0·00563	11560	P	0·929	0·983	0·999

Mean k_A by method G = $1·011 \times 10^{-4}$.
Mean k_A by method P = $1·003 \times 10^{-4}$.
Final mean k_A in chloride solutions = $1·007 \times 10^{-4}$.

* First three analyses from second part of Table III.

TABLE V.

$Cp(NO_3)_2$ in water at 25·00° C. (a = 0).

b.	x.	t.	Method.	$10^4k_A'' \equiv 10^4k_A'$.	10^4k_A.
0·00712	0·00192	3102	G	1·013	1·015
0·01157	0·00302	3073	G	0·979	0·981
0·01265	0·00302	3078	G	0·982	0·984
0·00888	0·00439	6805	G	1·003	1·009
0·00995	0·00486	6840	G	0·980	0·987
0·01187	0·00184	1705	P	0·994	0·994
	0·00443	4620	P	1·010	1·014
0·01185	0·00530	5882	P	1·009	1·014
	0·00622	7362	P	1·011	1·019

Mean k_A by method G = 0·995 × 10^{-4}.
Mean k_A by method P = 1·010 × 10^{-4}.
Final mean k_A in nitrate solution = 1·003 × 10^{-4}.

(d) Temperature Coefficient of k_A.

For the measurement of the temperature coefficient, $Cp(NO_3)_2$ was used throughout, and the experiments confined to the early stages of the reaction so that the correction for k_D was very small. The results in sub-section (a) indicate that the temperature coefficient of k_D is roughly two for five degrees at ionic strengths not very different from 0·05, so that with the corresponding value 1·95, as found, for the temperature coefficient of k_A, the assumption

$$\alpha = k_D/k_A \simeq 4$$

is valid over a small range of temperatures and ionic strengths. On this basis, the correction for k_D was always less than 1 per cent., and only occasionally greater than 0·5 per cent., in the experiments described in this sub-section. The point as to how far the rate in 0·01M $Cp(NO_3)_2$ may be taken to represent the rate at infinite dilution is discussed in section 5. The results of measurements of k_A at temperatures from 20·00° C. to 30·00° C. inclusive, are shown in Table VII. As the correction for k_D was so small, only the corrected constants are quoted.

TABLE VI.

$CpClO_4)_2$ in water at 25·00° C. $a = 0, b = 0·01117$.
Method P.

x.		$10^4k_A' \equiv 10^4k_A''$.	10^4k_A
0·00248	2505	1·003	1·004
0·00373	4150	0·979	0·981
0·00391	4420	0·975	0·978

Mean k_A in perchlorate solutions = 0·988 × 10^{-4}.

(e) Effects of Added Electrolytes.

Table VIII. summarises the results obtained. The constants are mean values from several determinations. To correct for de-aquotisation values of k_D were obtained by interpolation or (short) extrapolation from the values given in sec. (a) on a plot of log k_D against μ. The correction is very small: usually less than 1 per cent. The results at high ionic strengths are not corrected, $i.e.$ k'' is given.

TABLE VII.

$Cp(NO_3)_2$ in water at various temperatures. (a = 0.)

Temp. (°C).	b.	x.	t.	$10^4 k_A$.	Mean $10^4 k_A$.
20·00	0·00825	0·00253	7245	0·506	0·510
		0·00290	8400	0·517	
	0·01303	0·00395	7126	0·508	
		0·00444	8265	0·506	
		0·00459	8520	0·512	
22·50	0·00782	0·00262	5790	0·707	0·714
	0·01257	0·00329	4245	0·716	
		0·00505	7140	0·723	
27·50	0·01420	0·00268	1480	1·414	1·400
		0·00402	2395	1·392	
		0·00604	4000	1·391	
	0·01192	0·00232	1530	1·416	
		0·00372	2685	1·394	
		0·00513	4060	1·393	
30·00	0·01361	0·00244	1021	1·938	1·951
	0·01140	0·00321	1671	1·980	
		0·00643	4298	1·952	
	0·00928	0·00245	1590	1·928	
		0·00537	4430	1·968	

TABLE VIII.—SALT EFFECTS.

Solution.*		Effective Anion.	Conc. of Anion.	$10^4 k_A$ (at 25·00° C.).
$Cp(NO_3)_2$,	0·01 M	NO_3—	0·02	1·003
,, + KNO_3,	0·2 M	,,	0·22	1·08
,, + KNO_3,	0·1 M	,,	0·12	1·07
,, + HNO_3,	0·17 M	,,	0·19	1·08
,, + $Lu(NO_3)_3$,	0·026 M	,,	0·08	1·06
$CpCl_2$ + KNO_3,	0·1 M	,,	0·1	1·06
,, ,,	0·05 M	,,	0·05	1·03
$Cp(NO_3)_2$ + $HClO_4$,	0·27 M	ClO_4—	0·27	0·87
,, ,,	0·2 M	,,	0·2	0·89
,, ,,	0·08 M	,,	0·08	0·93
$Cp(ClO_4)_2$,	0·04 M	,,	0·08	0·94
$Cp(NO_3)_2$ + $Lu(ClO_4)_3$,	0·0135 M	,,	0·04	0·99
$Cp(ClO_4)_2$,	0·01 M	,,	0·02	0·99
$Cp(NO_3)_2$ + $KClO_3$,	0·2 M	ClO_3—	0·2	1·05
,,	0·1 M	,,	0·1	1·02
$CpCl_2$ + CH_3COONa + a little CH_3COOH	0·3 M	CH_3COO—	0·3	1·49
,, + $HCOONa$ + a little $HCOOH$	0·2 M	$HCOO$—	0·2	1·18
$Cp(NO_3)_2$ + H_2SO_4	0·1 M	?	?	1·41 †
,, + K_2SO_4	0·2 M	?	?	2·35
,, + ,,	0·1 M	?	?	2·02
,, + $KHSO_4$	0·2 M	?	?	2·18
,, + ,,	0·1 M	?	?	1·91

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* Except where otherwise stated, the Cp salt is at a concentration of about 0·01 M.

† These are uncorrected constants, $k_A'' \times 10^4$.

5. Discussion.

The validity of the assumptions of Section 3, and of the method of allowing for the reversibility of the reaction, is shown by the results in Tables II. to VI. inclusive. The fact that the rates in dilute solutions of chloropentammine chloride and nitrate are identical within the experimental error suggests that these are the same as that at infinite dilution. As, however, nitrate ions are found to accelerate the reaction it may appear that the rate in even dilute chloropentammine nitrate may be appreciably higher than that at infinite dilution. Since perchlorate ions decelerate the reaction to roughly the same extent the rate at infinited dilution may be supposed to be a mean between those observed in dilute solutions of the nitrate and the perchlorate, *i.e.*, about $0·996 . 10^{-4}$. If the small difference between this and the observed rate in the nitrate is real, then it appears that the rate in chloride solution, which is slightly higher still, must show the influence of an accelerating effect of the chloride ion. It did not appear practicable to test this point by using higher concentrations of chloride ions as this would enormously increase the experimental error. In any case the rate at infinite dilution appears to differ from that in M/100 $Cp(NO_3)_2$ by less than 1 per cent., if at all.

From the data of Tables V. and VII. the following values are obtained for the temperature coefficient:

$k22·5°/k20°$	$k25°/k22·5°$	$k27·5°/k25°$	$k30°/k27·5°$	Mean
1·400	1·405	1·396	1·393	1·399 per 2·5° C.

and thus $k_A = Ze^{-E/RT} = 2·4 \times 10^{13} \times e^{-28,700/RT}$.

In Table IX. these values of Z and E are compared with others computed by the author from the few available data on analogous reactions.

TABLE IX.—COMPARISON WITH OTHER AQUOTISATION REACTIONS.

Reaction.	*Z.*	*E.*	References.
$(Co . 5NH_3 . NO_3) + H_2O$	$2·5 \times 10^{15}$	24,800	(8)
$(Co . 4NH_3 . H_2O . NO_3) + H_2O$	$9·6 \times 10^{15}$	24,900	(8)
$(Cr . 5NH_3 . Cl) + H_2O$	$4·3 \times 10^{12}$	21,600	(9)
$(Cr . 5NH_3 . Br) + H_2O$	$3·9 \times 10^{13}$	22,000	(10)
$(Co . 5NH_3 . Cl) + H_2O$	$2·4 \times 10^{13}$	23,700	Present investigation

Any conclusions drawn from these numbers must be regarded as tentative, as the present investigation is the only one in which the rate was studied at more than two temperatures, and in which the reverse reaction was taken into account. However, it is probably significant that the three halogeno-ions give similar Z-terms (within the very reasonable factor of six) irrespective of whether the central atom is Cr or Co, whereas even when the central atoms are identical, halogeno- and nitrato-ions give Z-terms differing a hundred-fold. On the other hand if the rather small differences are to be regarded as real the critical increments appear to be specific for each of the combinations Co—NO_3, Co-halogen, and Cr-halogen.

As regards the salt effect, the results given in Table VIII. show that this depends on the nature and concentration of the anion, but is independent of the kations or of the total ionic strength of the solution.

At higher concentrations the effect is not linear. It is positive in all cases studied except with perchlorates.

It is important to note that the rate is the same in acid as in neutral solutions when the same anions at the same concentrations are present: this shows that the relatively rapid reaction

$$Cp^{2+} + OH^- \rightarrow (Co . 5NH_3 . OH)^{2+} + Cl^-$$

is playing no part in the aquotisation reaction.

The question of the rate at infinite dilution has already been referred to.

It is possible that part or all of the positive salt effect may be due to a replacement reaction such as

$$(Co . 5NH_3 . Cl)^{2+} + NO_3^- \rightarrow (Co . 5NH_3 . NO_3)^{2+} + Cl^-,$$

followed presumably by aquotisation of the new acido-complex. This question must be left open for the time being. It is proposed to make a more detailed investigation of these salt effects in the near future.

Summary.

The velocity of aquotisation of the chloropentammine cobaltic ion has been studied at a series of temperatures and in presence of added electrolytes, by determination of the free chloride ion.

The reaction has the character of a unimolecular reaction opposed by a bimolecular reaction.

The rate of the forward reaction, and its dependance on temperature, may be expressed by $k = 2 \cdot 4 \times 10^{13} \times e^{-23,700/RT}$.

The salt effects are specific, depending on the nature of the anion, and are positive in all cases studied except with perchlorates.

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[8] Bronsted, *Z. physikal. Chem.*, 1926, **120**, 383

[9] Freundlich and Pape, *ibid.*, 1914, **86**, 458.

[10] Freundlich and Bartels, *ibid.*, 1922, **101**, 177

RELATIONS BETWEEN THE ENERGY AND ENTROPY OF SOLUTION AND THEIR SIGNIFICANCE.

By R. P. Bell.

Received 2nd February, 1937.

The transfer of a molecule from the gas phase to a solution is completely characterised from a thermodynamic point of view by the change in any two of the three partial molal quantities heat content ($\bar{H}$), free energy ($\bar{F}$) and entropy ($\bar{S}$), these changes being related by the equation

$$\Delta\bar{F} = \Delta\bar{H} - T\Delta\bar{S} \quad . \quad . \quad . \quad . \quad (1)$$

A complete molecular model of the solute and solvent would give an *a priori* prediction of all the quantities involved, but this is not yet possible even for the simplest actual cases. However, if we consider a series of systems in which the forces acting are qualitatively similar, it might be possible to derive a further relation between $\Delta\bar{F}$, $\Delta\bar{H}$ and $\Delta\bar{S}$ which would be valid for any system in this series, and would thus make a knowledge of one of these quantities sufficient to determine the other two. Such relations might be of two kinds, namely

(*a*) A relation valid for a given solute in a series of different solvents ;

or

(*b*) A relation valid for a series of different solutes in the same solvent.

Evans and Polanyi[1] have recently suggested that such relations might exist, and have examined the available experimental data for the solubility of solids in liquids. They come to the conclusion that a relation of type (*a*) is valid, this relation having the simple form

$$T\Delta\bar{S} = \alpha\Delta\bar{H} + \beta \quad . \quad . \quad . \quad . \quad (2)$$

where $\Delta\bar{S}$ and $\Delta\bar{H}$ refer to the solution of the same solute in a series of different solvents, and α and β are independent of the solvent. On the other hand, the corresponding relation for a series of different solutes in the same solvent was found to be of only very limited validity.

All the solutes considered by Evans and Polanyi are substances of fairly high molecular weight which are solid or liquid at ordinary temperatures. It is therefore of interest to analyse the data for the solubility of gases, especially as the approximate regularity already pointed out by Lannung[2] indicates the existence of some relation analogous to (2).

For sufficiently dilute solutions $\Delta\bar{H}$ is independent of the concentration of solute in either phase, while $\Delta\bar{S}$ and $\Delta\bar{F}$ depend on the ratio of the concentrations in the gas and the solution. We shall take as standard conditions the case in which the solute is present at equal volume concentrations in the liquid and vapour phases. (The reasons for employing volume concentrations rather than any other concentration scale has already been dealt with fully.)[3] Then, if λ is the Ostwald solubility coefficient and v_s the volume of a fixed quantitity of solvent, we have

$$\Delta\bar{F} = -RT\log\lambda \quad . \quad . \quad . \quad . \quad (3)$$

$$\Delta\bar{H} = RT^2\left\{\frac{\mathrm{d}\log\lambda}{\mathrm{d}T} + \frac{\mathrm{d}\log v_s}{\mathrm{d}T}\right\} - RT \quad . \quad . \quad . \quad (4)$$

so that $\Delta\bar{F}$, $\Delta\bar{H}$ and $\Delta\bar{S}$ can all be found from solubility measurements at different temperatures and the coefficient of expansion of the solvent.

A large proportion of the older work on gas solubilities is of doubtful accuracy, or covers a temperature range too small for present purposes. We have therefore confined our attention to the accurate work of Horiuti[4] on the solubilities of a number of gases in five solvents over a large temperature range, and the work of Lannung[2] on the solubilities of the rare gases. (It may be remarked that the inclusion of less reliable data serves to confirm the conclusions reached here within the uncertainty of the values obtained.) The values of $\Delta\bar{F}$, $\Delta\bar{H}$ and $T\Delta\bar{S}$

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[1] *Trans. Faraday Soc.*, 1936, **32**, 1333.

[2] *J. Amer. Chem. Soc.*, 1930, **52**, 68.

[3] R. P. Bell and O. Gatty, *Phil Mag* (7), 1935, **19**, 66.

[4] *Sci. Papers Inst. Phys. Chem Res. Tokyo*, 1931, **17**, 125.

TABLE I.

Solute.	$\Delta\bar{F}$.	$\Delta\bar{H}$.	$T\Delta\bar{S}$.	$T\Delta\bar{S}$ (calc.).
CCl_4 ($T\Delta\bar{S} = 0{\cdot}364\ \ \Delta\bar{H} - 0{\cdot}645$.)				
H_2 .	1·44	1·22	−0·22	− 0·20
N_2 .	1·06	0·57	−0·49	− 0·44
O_2 .	0·69	0·00	−0·69	− 0·65
CO .	0·83	0·32	−0·51	− 0·53
N_2O .	−0·87	−2·47	−1·60	− 1·55
CH_4 .	0·18	−0·72	−0·90	− 0·91
C_2H_2 .	−0·65	−2·12	−1·47	− 1·42
C_2H_4 .	−0·78	−2·10	−1·32	− 1·41
C_2H_6 .	−1·00	−2·48	−1·40	− 1·55
C_6H_6 $T\Delta\bar{S} = 0{\cdot}425\ \ \Delta\bar{H} - 0{\cdot}61$.)				
He .	2·25	2·71	0·46	0·52
Ne .	2·01	2·56	0·55	0·45
A .	0·82	0·86	−0·04	− 0·24
H_2 .	1·51	1·50	−0·01	− 0·03
N_2 .	1·23	0·91	−0·32	− 0·22
O_2 .	0·87	0·36	−0·51	− 0·46
CO .	0·99	0·49	−0·50	− 0·40
N_2O .	−0·78	−2·17	−1·39	− 1·53
CH_4 .	0·33	−0·42	−0·75	− 0·79
C_2H_2 .	−0·94	−2·87	−1·93	− 1·83
C_2H_4 .	−0·73	−1·96	−1·23	− 1·44
C_2H_6 .	−0·84	−2·01	−1·57	− 1·47
C_6H_5Cl ($T\Delta\bar{S} = 0{\cdot}342\ \ \Delta\bar{H} - 0{\cdot}84$.)				
H_2 .	1·60	1·22	−0·38	− 0·42
N_2 .	1·30	0·60	−0·70	− 0·64
O_2 .	0·96	0·10	−0·86	− 0·84
CO .	1·09	0·34	−0·75	− 0·72
N_2O .	−0·69	−2·46	−1·77	− 1·69
CH_4 .	0·42	−0·64	−1·06	− 1·06
C_2H_2 .	−0·76	−2·35	−1·59	− 1·64
C_2H_4 .	−0·63	−2·21	−1·58	− 1·60
C_2H_6 .	−0·76	−2·32	−1·56	− 1·63
Acetone. ($T\Delta\bar{S} = 0{\cdot}440\ \ \Delta\bar{H} - 0{\cdot}47$.)				
He .	1·96	3·24	1·28	0·95
Ne .	1·73	1·96	0·23	0·39
A .	0·70	0·74	0·04	− 0·14
H_2 .	1·34	1·22	−0·12	0·07
N_2 .	0·99	0·62	−0·37	− 0·20
O_2 .	0·74	0·30	−0·44	− 0·34
CO .	0·78	0·31	−0·47	− 0·33
N_2O .	−1·06	−2·87	−1·81	− 1·73
CH_4 .	0·28	−0·42	−0·70	− 0·66
C_2H_2 .	−1·82	−3·75	−1·93	− 2·11
C_2H_4 .	−0·77	−1·89	−1·12	− 1·30
C_2H_6 .	−0·70	−1·97	−1·27	− 1·34
M. Acetate. ($T\Delta\bar{S} = 0{\cdot}400\ \ \Delta\bar{H} - 0{\cdot}57$.)				
H_2 .	1·38	1·22	−0·16	− 0·08
N_2 .	0·99	0·65	−0·34	− 0·31
O_2 .	0·75	0·30	−0·45	− 0·45
CO .	0·78	0·31	−0·47	− 0·45
N_2O .	−1·09	−2·89	−1·80	− 1·73
CH_4 .	0·29	−0·36	−0·65	− 0·71
C_2H_2 .	−1·81	−4·08	−2·27	− 2·20
C_2H_4 .	−0·75	−1·98	−1·23	− 1·36
C_2H_6 .	−0·70	−1·98	−1·28	− 1·36

are given in kilocalories per gram-molecule in the first three columns of the table. The temperature is throughout 20° C.

Examination of these data shows that for a given solvent there is a linear relation between $T\Delta\bar{S}$ and $\Delta\bar{H}$ (*cf.* equation 2) for the different solutes considered. The equations valid for each solvent are given at the head of each section of the table, and the values of $T\Delta\bar{S}$ calculated from these equations are given in the last column. Both in range and in accuracy the agreement between the observed and calculated values is comparable to that found by Evans and Polanyi, and it may be noted that the mean value of the constant α (0·39) is nearly the same as the mean value they obtained (0·37) for a given solute in a series of solvents.

If, on the other hand, we consider the data in the table opposite relating to a single gas in different solvents, there appears to be no relation between $T\Delta\bar{S}$ and $\Delta\bar{H}$, in contrast to the behaviour of solutes of higher molecular weight.*

The following facts therefore emerge :—

(1) For solutes of high molecular weight (solids and liquids) there is a functional relationship between the entropy of solution and the heat of solution of a given solute in a series of solvents, but there is no such relationship for a series of solutes in a given solvent.

(2) For solutes of low molecular weight (gases) the position is reversed, *i.e.*, there is a functional relationship between entropy of solution and heat of solution for a series of solutes in a given solvent, but no such relationship exists for a given solute in a series of solvents.

(3) Such relationships are linear, and the factor α in equation (2) is positive and less than unity.

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* The data in the table relating to a single solute do not cover a very wide range of values of $T\Delta\bar{S}$ and $\Delta\bar{H}$, but the same conclusion is reached if the range is extended by including less accurate data.

Evans and Polanyi have shown that there is a close analogy between relationships of this kind, and formally similar relationships valid in other fields (*e.g.*, reaction kinetics). They do not, however, attempt any interpretation in terms of molecular theory, and in particular their treatment does not suggest any reasons for the differences observed between solutes of high and low molecular weight. We shall therefore investigate how far the facts can be accounted for in terms of molecular interaction.

The thermodynamic quantities measured depend ultimately on the forces between the solvent and solute molecules, and we should anticipate that the data for a series of solutions will be expressible by a single relationship only when the same *type* of intermolecular force operates throughout. This condition may be expressed more precisely by saying that when a solute molecule and a solvent molecule are a given distance apart, the variations in their mutual potential energy as we pass from one system to another must be expressible by variations of a single parameter. For the majority of pairs of molecules the dispersion forces are by far the most important, even in cases when considerable dipole moments are present,[5] so that the above condition will be satisfied for most non-electrolyte solutions.*

Uniformity in the type of intermolecular force is not, however, the sole condition necessary for the existence of a relation between $\Delta\bar{H}$ and $T\Delta\bar{S}$. The latter quantities are obtained from the intermolecular energies by two different kinds of averaging processes: this is expressed by the general statistical equations for the contribution of molecular interaction to the energy and entropy of a system of n molecules,

$$\left.\begin{aligned} H &= \frac{\int \ldots \int^{v} \epsilon e^{-\epsilon/kT}\, dv_1 \ldots dv_n}{\int \ldots \int^{v} e^{-\epsilon/kT}\, dv_1 \ldots dv_n} \\ F = H - TS &= -kT \log \frac{\int \ldots \int^{v} e^{-\epsilon/kT}\, dv_1 \ldots dv_n}{\int \ldots \int^{v} dv_1 \ldots dv_n} \end{aligned}\right\} \quad . \qquad (5)$$

where $dv_1 \ldots dv_n$ represent the elements of phase space necessary to specify the position of each molecule, ϵ is the energy corresponding to a particular configuration, and the integration extends over the whole volume occupied by the system. If we consider a system consisting of one solute molecule in a given volume of solvent, then the partial molal quantities we have been dealing with are obtained by evaluating the values of H and TS for this system, and subtracting the corresponding quantities for a system consisting of the solvent alone. For a condensed system such as a liquid the value of ϵ is a very complicated function of the various co-ordinates, and even in a series of systems in which the variations of intermolecular force can be represented by a single parameter, it will in general be necessary to introduce a further factor representing the way in which the nature of the averaging process is affected by the geometrical properties of the system (*e.g.*, the shape and relative size of the solute and solvent molecules). A simple instance of this is the hypothetical case in which there are no attractive forces between the solvent and solute molecules, and the repulsive forces can be representing the molecules as rigid spheres : * for such a system the entropy of solution will obviously contain a positional term which will depend on the individual geometry of the system, and will not be related to the energy of solution. In other words, we cannot in general assume either that a given solvent constitutes a fixed phase space for different solutes, or that a given solute constitutes a fixed phase space for different solvents.

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[5] *Cf.* F. London, *Z. Physik*, 1930, **63**, 245.

* Small molecules containing the hydroxyl group constitute one of the few cases in which dipole forces are of importance, and it may be noted that the data for water and the aliphatic alcohols as solutes do not fit into the relationships given above. On the other hand, it has been shown by Butler (*Trans Faraday Soc.*, 1937, **33**, 171, 229) that there is a linear relation between $\Delta\bar{H}$ and $\Delta\bar{S}$ for ten alcohols in water, and for four alcohols in benzene: this presumably indicates that within this group of molecules the relative importance of dipole and dispersion forces is roughly constant.

In particular cases, however, it may be legitimate to assume that the configuration of the solvent molecules is not appreciably disturbed by the presence of a solute molecule (or, at least, that it is disturbed in the same way by different solute molecules) : this will be the case *if the interaction is small and the solute molecule is considerably smaller than the solvent molecule.*† All probable configurations of a given solvent will then be equivalent, and we can choose a particular configuration as a fixed phase space for a series of solutes satisfying the above condition. This leads to the expressions

$$\left.\begin{aligned} \bar{H} &= \frac{\int^{v} \epsilon(v_s, \lambda)\, e^{-\epsilon(v_s, \lambda)/kT} \mathrm{d}v_s}{\int^{v} e^{-\epsilon(v_s, \lambda)/kT} \mathrm{d}v_s} \\ \bar{F} = \bar{H} - T\bar{S} &= kT \log \frac{\int^{v} \epsilon^{-\epsilon(v_s, \lambda)/kT} \mathrm{d}v_s}{\int^{v} dv_s} \end{aligned}\right\} \quad . \quad . \quad (6)$$

where $\mathrm{d}v_s$ is an element of the phase space defining the position of the solute molecule, λ is the single parameter characterising the interaction between the solute and solvent molecules, and the form of $\epsilon(v_s, \lambda)$ depends on the solvent but not on the solute. Since the limits of integration are the same throughout, for a series of solutes in the same solute $\bar{H}$ and $T\bar{S}$ are thus both unique functions of the parameter λ, and hence there is a functional relationship between them. On the other hand, variations of solvent correspond to variations in the form of $\epsilon(v_s, \lambda)$, and there will not in this case be any such relationship. These results correspond exactly to what has been found for solutions of gases, where the solute molecules are, in fact, smaller than the solvent molecules and the total interaction is small.

The above treatment does not apply to the large solute molecules treated by Evans and Polanyi, agreeing with the fact that no relationship was found by them for different solutes in the same solvent. On the other hand, we have not been able to account satisfactorily for the relations which exist for a given large solute molecule in different solvents. It may, however, be noted that in the extreme case when the solute molecule is much larger than the solvent molecule, the latter can be envisaged as a continuous medium, and the positional entropy of the solute is the same as in a gas of the same volume. This simplified picture will lead to the required result if certain assumptions are made about the macroscopic properties of the continuous medium : these assumptions cannot be directly derived on a molecular basis, but show some analogy to empirical generalisations for pure liquids such as Trouton's rule. However, the solute molecules considered by Evans and Polanyi hardly satisfy these conditions, since they are in many cases only slightly larger than the solvent molecules. If (as we believe) the difference in behaviour between solutions of gases on the one hand and of solids on the other hand is actually due to differences in relative molecular dimensions, there ought to be an intermediate class of systems obeying either both or neither of the relationships dealt with in this paper. Such systems would probably consist of mixtures of completely miscible liquids, for which there are only scanty data in the dilute range.

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* Such a system has been termed a "solution of limited interaction"; *cf* R. P. Bell and O. Gatty.[3]

† The importance of relative molecular size for interpreting the thermodynamic properties of solutions has been previously pointed out (Bell and Gatty, *loc. cit.*), and its effect on the entropy of solution has been recently discussed by Kirkwood (*Chem. Rev.*, 1936, 19, 274).

Summary.

It is shown on the basis of existing data for the solubility of gases that there is a linear relation between the energy and entropy of solution of different solutes in the same solvent. This result is compared and contrasted with the regularities found by Evans and Polanyi for solutions of solids, and an attempt is made to interpret the facts in terms of a statistical treatment of the intermolecular forces.

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THE PHOTOCHEMISTRY OF POLYATOMIC MOLECULES CONTAINING ALKYL RADICALS. IV. MERCURY DIMETHYL.

By J. W. Linnett and H. W. Thompson.

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In three previous papers measurements on the ultra-violet absorption spectra of a series of polyatomic molecules containing alkyl radicals have been described.[1] These measurements were made with a view to correlating the spectral data with measurements on the corresponding photochemical decompositions. The present paper deals with the photolysis of mercury dimethyl, the spectrum of which consists of diffuse bands below 2150 Å., with an overlapping continuum which may extend as far as 2600 Å. The present measurements were made with light of wave-length near the long wave limit of the continuum.

Two recent cognate papers should be mentioned. Terenin and

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[1] (I) *J. Chem. Soc.* 1934, p. 790 ; (II) *Proc. Roy. Soc. A*, 1935, 150, 603 ; (III) *Proc. Roy. Soc. A*, 1936, 156, 108.

Prileshajeva [2] have attempted to detect the presence of free methyl radicals in the vapour of mercury dimethyl when irradiated by light of wave-length 2100 Å., by passing the vapours over metallic mirrors. The experiments led to the conclusions that free radicals were present, but no quantitative measurements were made.

Leighton and Mortensen [3] have examined the photolysis of lead tetramethyl both in the gas phase and in solution. In the gas phase the quantum efficiency is 1·11, and is reduced towards unity in the presence of air. The authors conclude that the bulk of the reaction can be represented by the equation

$$\mathrm{Pb\ R_4} \rightarrow \mathrm{Pb} + 2\mathrm{R_2}$$

Some free radicals were, however, detected.

The present work shows that when the vapour of mercury dimethyl is illuminated by light of wave-length 2537 Å., the bulk of the gaseous products is ethane, with much smaller proportions of other hydrocarbons. The quantum yield is in the neighbourhood of unity. The facts appear to be best interpreted by supposing that the primary act is

$$\mathrm{Hg(CH_3)_2} + h\nu = \mathrm{Hg} + \mathrm{C_2H_6}$$

with the simultaneous occurrence of a primary process giving free radicals and the possibility of a few reaction chains, so as to lead to an effective quantum yield of the order unity, and to subsidiary hydrocarbons other than ethane.

Experimental.

The mercury dimethyl was a Fraenkel and Landau product which had been purified by fractional distillation *in vacuo*, as for the spectroscopic work. Its purity had been tested previously by vapour pressure measurements.[4] The experimental work concerned for the most part two independent matters: (1) The analysis of the products of the photolysis, (2) the determination of the quantum yield.

In the analysis of the gaseous products of the photolysis the main difficulties arose partly from the necessity of first removing undecomposed mercury dimethyl, and also from the small volume of hydrocarbon product obtainable. The latter is unavoidable owing to the low vapour pressure of mercury dimethyl at the temperatures so far used. The only satisfactory method found for the removal of mercury dimethyl was solidification of the latter in a carbon dioxide-acetone freezing mixture, the temperature of which is about 50° C. below the melting-point of mercury dimethyl but still above the boiling-point of both ethane and methane. The apparatus for the collection of a sample of the gas is shown in Fig. 1. The vapour of mercury dimethyl was introduced into the quartz reaction cell A from the bulb C containing the liquid sample. B was a drying tube containing phosphorus pentoxide which could be connected to the apparatus by opening a tap, and D was a mercury manometer. After illumination, the gaseous products and residual mercury dimethyl vapour were slowly withdrawn into the container F by lowering the mercury reservoir G, and in the withdrawal passed through the trap E, cooled in a carbon dioxide-acetone freezing mixture. By reversing the tap H the gas in F (freed from mercury dimethyl) was driven over into the evacuated bulb I. H was then again reversed and the process of withdrawal repeated until all the gas had been removed from A. The vessel F, with I attached, was then disconnected from the rest of the apparatus at the ground flange J, and attached via this flange to the gas analysis apparatus. The gas was transferred to the latter from I by a Toeplar action using F, similar to the method used above for its withdrawal from the reaction cell. A known volume of the gas was then exploded with a measured volume of oxygen ; the change in volume after explosion was recorded and carbon dioxide determined by absorption in 33 per cent. caustic potash.

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[2] *Trans. Faraday Soc.*, 1935, 31, 1483.
[3] *J. Amer. Chem. Soc.*, 1936, 58, 448.
[4] *Trans. Faraday Soc.*, 1935, 31, 1743.

In the determination of the quantum efficiency, the low vapour pressure of mercury dimethyl again led to difficulties. An oil manometer was finally used to measure small pressures. The method adopted for determining the extent of the decomposition was as follows. The total pressure of mercury dimethyl was measured before and after illumination. The two readings usually agreed closely. The cell containing mercury dimethyl vapour, and the reaction products, was then surrounded by a solid carbon dioxide-acetone freezing mixture, and the ethane and methane pumped off. After the cell had again warmed up to room temperatures the pressure of residual mercury dimethyl was determined, and the difference between this and the pressure in the cell after illumination gave the pressure of ethane and methane produced. The apparatus is shown in Fig. 2. The quartz reaction cell was arranged as previously described. The oil manometer was a capillary U-tube EF, the oil being introduced from the reservoir G in which it had previously been warmed *in vacuo* to remove dissolved gas. Before each measurement of the pressure both sides of the manometer were evacuated through H and I, and then a pressure of air less than that to be measured was introduced into the limb E to act as a buffer against the mercury dimethyl vapour, which was slowly dissolved by the oil. The tap I was opened for three minutes and the levels of the oil in the two limbs measured. Previous experiments showed that in the three minute interval the oil came to equilibrium and during this period there was no appreciable diffusion of the vapour through the capillary tube to the surface of the oil. In order to calculate the number of molecules of ethane (the predominant product) formed, it was necessary to know the volume of the cell A and connecting tubes, and also the temperature. The latter was measured on a thermometer placed alongside the reaction cell, and the former by a previous experiment in which air was partitioned between A and a known volume.

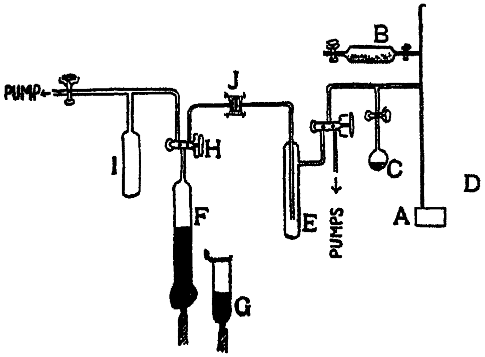

FIG. 1.

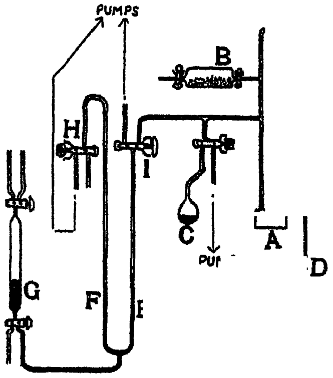

FIG. 2.

The light used for the photochemical work was in the region of 2537 Å., being filtered out from the radiation of a mercury lamp by a solution of nickel and cobalt salts with a 3 cm. layer of chlorine gas as described by

Bowen.[5] The mercury lamp was allowed to run hot and "reversal" of the resonance line undoubtedly occurred. The number of quanta transmitted through the cell before, during, and after the run was measured by the method of Leighton and Forbes.[6] The actinometric solution contained 1·65 gms. of uranyl oxalate, and 0·51 gms. of oxalic acid per litre. The quantum yield of the sensitised decomposition in this region was taken as 0·60. The oxalic acid decomposed was determined by titration with approximately $N/50$ potassium permanganate solution, which had been standardised against sodium oxalate.

Results.

On illumination, mercury dimethyl vapour gives rise to gaseous products, and after several runs in the same vessel a solid deposit is noticed which can be easily removed by concentrated nitric acid. The deposit has both the appearance and properties of metallic mercury.

The comparative absence of pressure change on illumination suggests at once that ethane may be the most important product of the photolysis, being formed according to the equation :—

$$Hg(CH_3)_2 = Hg + C_2H_6.$$

This is borne out by the analysis of the gaseous products, examples of which are given in Table I.

TABLE I.

Initial Volume *A*.	Contraction *B*.	Carbon Dioxide *C*.	*B/A*.	*C/A*.	Percentage of—		
					Methane.	Ethane.	Ethylene.
2·87	6·99	5·46	2·44	1·90	10	88	2
1·83	4·47	3·53	2·44	1·93	7	88	5
1·07	2·62	2·06	2·45	1·93	7	90	3
1·88	4·60	3·54	2·45	1·90	10	90	0

Explosion of ethane with excess oxygen gives a contraction of 2½ times the original volume of ethane, and a volume of carbon dioxide of 2 times. With methane the contraction is 2 times, and the carbon dioxide equal to, the original volume of methane. The mean contraction observed in the present case was about 2·45 times, and the carbon dioxide 1·92 times, the volume taken. Various facts suggest that the main subsidiary products are methane and ethylene, with perhaps an almost negligible amount of hydrogen. Assuming this to be true, the percentages of methane, ethane, and ethylene in the gaseous products can be calculated. The data are given in Table I., from which it is seen that the mean values are ethane 89 per cent., methane 8·5 per cent., and ethylene 2·5 per cent. This gives as an equation for the complete change

$$96\ Hg(CH_3)_2 = 89\ C_2H_6 + 8{\cdot}5\ CH_4 + 2{\cdot}5\ C_2H_4 + 96\ Hg$$

in which the two sides balance almost exactly. This implies that about 93 per cent. of the mercury dimethyl decomposes giving ethane.

The mixture $(xCH_4 + yC_2H_6 + yH_2)$ would behave, as far as the combustion data are concerned, like $(x + 2y)CH_4$. Hence it is possible that the hydrocarbon products may contain rather less methane than indicated above. If this were so, however, it would simply imply a still greater percentage of ethane, with a little hydrogen and a decreased percentage of methane. This ambiguity is, however, of minor significance, and does not interfere with the main conclusion that over 90 per cent. of the hydrocarbon products consists of ethane.

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[5] *J. Chem. Soc.*, 1932, 2236; 1934, 76.

[6] *J. Amer. Chem. Soc.*, 1930, 52, 3139.

The above equation provides for a pressure increase in the photolysis of about 3 per cent. The observed pressure increase was occasionally greater, and sometimes less than this. The differences are probably to be explained by variable adsorption or desorption of the mercury dimethyl from the vessel walls. It was noticed that when the vapour was first introduced into the evacuated reaction vessel, a small pressure decrease could be observed, which was presumably due to slight adsorption on the surface. This matter is, however, of minor significance.

The following is a typical series of measurements on one determination of the quantum yield.

The number of cubic centimetres of *N*/50 potassium permanganate equivalent to the oxalic acid decomposed by the light transmitted in forty minutes by the cell when evacuated before the run was 2·99 (mean of 5 readings). The corresponding reading using the evacuated cell after the run was 2·99 (mean of 5 readings). (The check at the end of a run was carried out in order to make certain that the very slight deposition on the front face during the small period of illumination was not causing a noticeable change in the light transmitted.) The corresponding reading during forty minutes of the run was 2·17 c.c. Thus the light absorbed was equivalent to 0·82 c.c. of *N*/50 potassium permanganate solution, which corresponds to 1·37 × 10^{-5} gm. mol. quanta.

Now the pressure of mercury before illumination was 312·5 mm. of oil, and after illumination was 313 mm. of oil, which is equivalent in both cases to 20·2 mm. mercury. After removal of the hydrocarbon gases the pressure of unchanged mercury dimethyl was 251 mm. of oil, or 16·2 mm. mercury. In the run therefore 4·0 mm. of mercury dimethyl had decomposed. The readings were made at 22° C. and the volume of the cell and connecting tubes was 66·5 c.c. Therefore the number of gram molecules of gaseous products was 1·44 × 10^{-5}. But according to the equation given above 96 vols. give rise to 100 vols. Hence we can say that the number of gram molecules of mercury dimethyl decomposed is 1·38 × 10^{-5}. This gives the quantum yield as 1·01.

Table II. summarises the results of several runs.

TABLE II.

Run No.	Initial Press. mm.	Final Press. mm.	Residual Press. ($Hg(CH_3)_2$).	Gm. Mol. $Hg(CH_3)_2$ Decomp. × 10^5.	Gm. Mol. Quanta. Abs. × 10^5.	Quantum Yield.
1	20·9	21·0	17·1	1·35	1·58	0·86
2	19·5	19·5	15·1	1·53	1·53	1·00
3	20·2	20·2	16·2	1·38	1·37	1·01
4	—	15·9	11·9	1·39	1·37	1·02
5	13·2	13·1	9·9	1·11	1·07	1·04
6	—	19·9	17·4	0·95	1·02	0·93
7	—	20·7	17·6	1·17	0·99	1·18
8	—	17·5	14·1	1·30	1·40	0·93

The mean of all the values obtained was 1·0, and it is clear that the quantum yield does not differ markedly from unity. Over the pressure range so far used, 10-25 mm., no detectable drift in the value of the quantum yield could be established.

Discussion.

The nature of the spectrum of mercury dimethyl suggests that the primary process on absorption of light in the ultra-violet region is a one-act dissociation. Three possibilities are open :—

(1) $Hg(CH_3)_2 + h\nu \rightarrow Hg + C_2H_6$
(2) $Hg(CH_3)_2 + h\nu \rightarrow Hg + CH_3 + CH_3$
(3) $Hg(CH_3)_2 + h\nu \rightarrow Hg(CH_3) + CH_3$

The facts which are established by the above experiments are —

(i) The quantum yield is unity within the range of experimental error.

(ii) Decomposition yields predominantly (93 per cent.) ethane, and small amounts of other hydrocarbons are simultaneously formed.

It seems justifiable to conclude at once that the bulk of the reaction follows the course (1), unless we suppose that the two methyl radicals formed in (2) re-unite to form ethane. Propagation of reaction chains by such free radicals would be expected to give rise to a high quantum yield on the one hand and considerably more subsidiary hydrocarbon products than are formed.

It is, however, possible that the small amounts of methane and ethylene found are produced when free radicals formed in processes (2) or (3) give rise to reaction chains. The number of such chains that are propagated must then be small.

The question arises as to whether the entire decomposition occurs via a process of sensitisation by excited mercury vapour absorbing the resonance line. It is unfortunate that no other frequency of the mercury arc is suitable for studying the decomposition. Actually the nature of the arc used suggests that this complication is not serious. The extinction coefficient of mercury dimethyl is moreover very high. It will be interesting to compare the present data with that obtained in the analogous decomposition of zinc dimethyl and other similar compounds where such sensitisation is not possible.

The experiments of Leighton and Mortensen[3] on the photolysis of lead tetramethyl and lead tetraphenyl appear to be parallel to the above, and the conclusions drawn from them are similar. In each of these cases the overall reaction is

$$Pb\,R_4 = Pb + 2\,R_2$$

the quantum yield with lead tetramethyl in the gas phase being between 1·0 and 1·11. Several independent observations led to the conclusion that a few free radicals were, however, present in the illuminated vapour, though their number was small.

The detection of free radicals in the irradiated vapours of mercury dimethyl and lead tetraethyl by Terenin and Prileshajeva[2] (*loc. cit.*) using the method of the disappearance of metallic mirrors, is not at all in contradiction with the above results. Strictly speaking, since the wave-lengths used by these workers were in the region of 2100 Å., the two sets of data are not directly comparable, and it is quite possible that a change in the mechanism of the decomposition occurs in passing to shorter wave-lengths. The qualitative method of Terenin and Prileshajeva does not at all establish the proportion of the reaction proceeding by a primary process of radical liberation. The quantitative photochemical data on the other hand not only show that the bulk of the decomposition avoids such a process, but also indicate that a small fraction of it may take this course. If the experiments of Terenin and Prileshajeva can be regarded as at all quantitative, they suggest that with wavelengths greater than about 2200 Å. the production of free radicals is less efficient.

We have attempted to detect the extent to which the reaction proceeds via a mechanism involving free radicals by an independent method. It has recently been found that the velocity of decomposition of certain organic compounds at high temperatures is noticeably diminished in the presence of small amounts of nitric oxide. There is considerable evidence for believing that this inhibiting influence is due to a reaction of the nitric oxide with free radicals of which the methyl radical is perhaps the most important. Accordingly the velocity and quantum yield of the photochemical decomposition of the metal alkyls might be decreased in the presence of nitric oxide. The effect would, however, probably be noticeable only at higher temperatures where the rate of reaction between nitric oxide and methyl radicals becomes appreciable. Measurements of this type are in progress, but they appear to be complicated by a photochemical reaction which occurs at room temperature between mercury dimethyl and nitric oxide. This reaction involves a pressure decrease, and pressure measurements suggest that for every molecule of mercury dimethyl reacting there disappear two to three molecules of nitric oxide, and a solid is formed. It is not yet clear whether the nitric oxide reacts with radicals or merely with excited mercury dimethyl molecules. The general features of this reaction are complex, and details will be given later.

Photochemical work with mixed metallic alkyls would throw additional light on the matter.

Summary.

The photochemical decomposition of mercury dimethyl vapour by light of wave-length 2537 Å. has been studied. The products are metallic mercury and a mixture of hydrocarbons of which ethane is by far the more predominant. The quantum efficiency of the decomposition is, within the limits of experimental error, unity. The facts are well explained by the hypothesis that the primary act is in general—

$$Hg(CH_3)_2 \rightarrow Hg + C_2H_6$$

without the production of reaction chains, but a few free radicals produced by the less important processes :—

$$Hg(CH_3)_2 \rightarrow Hg + CH_3 + CH_3$$

or

$$Hg(CH_3)_2 \rightarrow Hg(CH_3) + CH_3$$

may give rise to chains and to subsidiary hydrocarbon products.

We are grateful to the Government Grant Committee of the Royal Society, and to The Chemical Society, for grants towards the purchase of apparatus, and to the Department of Scientific and Industrial Research for a Maintenance Grant to one of us.

The Old Chemistry Department,
University Museum, Oxford.

REVIEWS OF BOOKS.

Collected Scientific Papers of Sir William Bate Hardy. (Cambridge University Press, 1936. Pp. 922. Price, £3 3s.)

Although this splendid volume has been published under the auspices of the Colloid Committee of the Faraday Society, the credit for the inception of the idea as well as for the obtaining of funds and the whole work of editing and seeing the volume through the press is due to Professor Eric K. Rideal. The result is one of those great landmarks in the development of science which every student ought to read, but for which, alas, in these hurried days of examinations and textbooks, so very few find time or opportunity.

The first fourteen papers show Hardy as a keen young biologist. He is chiefly interested in living cells, and especially in the " wandering cells." The title of the fourteenth, " On the structure of cell protoplasm," is highly significant. He is attacking the citadel of life, he knows where the secret mystery lies hidden. And then ? Read the titles of the next two papers—" On the Coagulation of Proteid by Electricity " ; " A Preliminary Investigation of the Conditions which determine the Stability of Irreversible Hydrosols." Hardy sees, and sees with the true vision of a great mind, that the study of " living protoplasm " demands a preliminary investigation of colloid phenomena, and especially of the colloid phenomena exhibited by the proteins. Papers 15-29 deal chiefly with these subjects. All the world knows that in this period of investigation Hardy made fundamental discoveries, the importance of which for physical chemistry, colloid science, and biology cannot be too strongly emphasised.

And now what comes ? Read the titles of papers 30 and 32 : " The tension of composite fluid surfaces and the mechanical stability of films of fluid " ; " The influence of chemical constitution upon interfacial tension." Hardy now sees, and again it is a vision of genius, that biological and colloid phenomena demand an intensive study of the properties and actions occurring at surfaces and interfaces. This was, in the main, the great group of problems to which he devoted the latter part of his investigations in pure science. They are dealt with chiefly in papers 30-57, and relate to a wide variety of topics—composite fluid surfaces, films, interfacial tension, the spreading of fluid films on water and solids, static friction, boundary lubrication, adhesion, adsorption. We owe to this period of Hardy's work the great discovery of molecular orientation at surfaces and interfaces. It has played a fundamental role in the later investigations of Langmuir, Adam, Harkins, and many others. The title of paper 52, " Molecular orientation in living matter," shows us that Hardy saw its importance in the micro-morphology of living tissue and living cells. His work on friction and lubrication constituted a pioneer attack on a problem of great importance for engineering science.

It is well known that in the latter part of his life Hardy directed the scientific research work of the Low Temperature Station at Cambridge, in which numerous and important investigations were carried out on the ripening, preservation, and transport of natural foodstuffs, *e.g.*, fruit, vegetables, fish, meat, etc. Some people regret that Hardy should have devoted so much of his time to " applied science," and other people on other occasions discourse learnedly on " the impact of science on society." Well, here was a great example of the impact of a master mind of science on the solution of practical problems possessing enormous importance for the good health, happiness and prosperity of society. Although under the inspiring guidance and direction of Hardy the numerous and very difficult problems were attacked and solved by the methods of " pure " science, very little of the published work appeared under his own name. Only two papers in the present volume bear witness to this side of his life's work. Their titles are : " Freie und gebundene Flüssigkeit in Gelen " ; " The Freezing-point of Yolk and White of Egg " (H. P. Hale, with a note by Sir William Hardy).

The work done at the Low Temperature Station on the vexed question of " free and combined water " in gels and colloid systems in general possesses great importance for colloid science and for biology.

This brief review may suffice to give some indication of Hardy's famous investigations on the physical chemistry and physics of those vastly simpler things which we call " dead," *i.e.*, " non-living " systems. But always and to the end he was a far-seeing biologist. It is very fitting that the last paper in the volume under review bears the title " To remind : a biological essay." This was the Abraham Flexner Lecture, delivered in 1931. It sums up, in many respects, his philosophical position as a biologist and simultaneously an investigator of physico-chemical phenomena. One of the concluding sentences of this profound essay is characteristic of him. Speaking of the " improbability " of living beings and of the present state of science in relation thereto, he says : " Is there any guess which comes within whooping distance of the shifts and tricks by which the primordial slime clothed itself in diffraction gratings to give the birds the colours they need in a tropical forest ? "

Every biologist should read this farewell message of one of the greatest minds and most beloved spirits of our time. It belongs to H. G. Wells' " World Encyclopædia."

F. G. D.

The Study of the History of Science. By G. Sarton. (London : Oxford University Press, 1936. Pp. 75. Price 6s. 6d.)

These slim volumes contain an amount of wisdom which is out of all proportion to their modest dimensions. Dr. Sarton is concerned, in these inaugural lectures, with the broader matters of scope and background as regards the subject-matter, and of outlook and equipment as regards the teacher and researcher. As the author rightly points out, the mathematician who would investigate the development of mathematical science in Ruritania in the fourteenth century may, without grave difficulty, obtain that necessary knowledge of the history and culture of Ruritania which shall give him a proper outlook. That is, assuming that he possesses the historical sense—not so common as a possession as might hastily be inferred from Dr. Sarton's remarks. But the historian who would write of the development of the mathematical sciences is in far worse case. If he has not already had some special training in whatever science he would investigate, it is almost impossible to acquire it *ad hoc*.

Any general reader may peruse Dr. Sarton's lectures with pleasure and profit, but he has widened immensely the scope of his addresses by adding thereto critical and annotated bibliographies which not only provide pointers for the ignorant, but give information which the expert may not disdain to employ. Odd little pieces of information emerge. How many of us realise that the compilation of the Royal Society's Catalogue of Scientific Papers was first suggested by Joseph Henry, the secretary of the Smithsonian Institution, or that complete sets of its ill-fated successor, the International Catalogue of Scientific Literature can still be obtained (or could, a year ago) by him who is willing to pay for them at the rate of £60 a set unbound, or £100 bound? Of very special interest, too, is the bibliography of the lives of 118 modern mathematicians.

The volumes are an addition of permanent value to the literature of history.

A. F.

The Theory of the Properties of Metals and Alloys. By N. F. MOTT and H. JONES. (International Series of Monographs on Physics. Oxford: Clarendon Press and Humphrey Milford, 1936. Pp. xiii and 326. 108 Diagrams. Price 25s. net.)

The theoretical treatment of metallic lattices presents greater difficulties than does that of ionic or homopolar crystals, and this work is a pioneer attempt to deal with the problem by the methods of wave mechanics. It is essentially a book for the mathematical physicist, the difficulties being considerable, but the physicist and metallurgist to whom this new field is unfamiliar will find much of interest in the conclusions reached by novel methods. The order-disorder change in solid metallic solutions has lent itself well to this treatment, and the results of the discussion throw light on changes in solid alloys which had long presented difficulties to the metallographer. By making use of the concept of " Brillouin zones," the authors find theoretical support for the Hume-Rothery rules, which account for certain characteristic phases which present themselves in allied systems of alloys by a constant ratio between the numbers of atoms and of valency electrons, thus bringing out resemblances between chemical formulæ which at first sight appear highly dissimilar. Another interesting chapter deals with the various types of cohesion, and it is shown that there is no sharp distinction between the metallic and the homopolar link. Electrical resistance, magnetic properties, and the colour of alloys are among the other subjects considered. The book is a very notable contribution to the literature of scientific metallurgy.

C. H. D.

ABERDEEN: THE UNIVERSITY PRESS

AN ELECTROLYTIC ETCHING METHOD FOR REVEALING THE MICROSTRUCTURE OF ELECTRODEPOSITED NICKEL.

By A. J. Krombholz.[1]

Received 26th November, 1936.

The usual and apparently the most satisfactory method so far discovered for revealing the microstructure of nickel consists in etching the metal with a solution of nitric acid in glacial acetic acid. Various concentrations of these two acids have been recommended as being most suitable. Thus, W. A. Mudge[2] proposed a solution of 50 c.c. of concentrated nitric acid in 50 c.c. of glacial acetic acid for the " flat " etching of nickel and nickel alloys. G. E. Gardam and D. J. Macnaughtan,[3] in their study on the effect of annealing on the microstructure of nickel deposits, employed a solution consisting of 600 c.c. nitric acid (sp. gr. 1·42), 300 c.c. glacial acetic acid, and 300 c.c. of water. W. Blum and C. Kasper[4] used glacial acetic acid to which sufficient nitric acid had been added (the amount being less than 1 per cent.) to attack the polished nickel surface.

These various concentrations of nitric and glacial acetic acid were tried in connection with a study on the structure of relatively thin deposits of electrolytic nickel undertaken by this laboratory. However, none of them proved to be entirely satisfactory. The structures developed by the chemical attack of these two acids often appeared dark and lacking in fineness of detail. Bad pitting and a very rapid attack of the edges of the nickel deposits was also frequently encountered, this being particularly annoying when dealing with relatively thin deposits. Furthermore, when the nickel was deposited on sheet copper cathodes, the nitric-glacial acetic acid solution would attack the copper basis metal very rapidly.

Because of these difficulties, the attempt was made to develop an electrolytic method whereby the microstructure of electrodeposited nickel could be revealed without encountering the undesirable results so frequently experienced with the method of direct chemical attack. For this purpose a considerable number of different electrolytes were investigated. In general, it was found that aqueous solutions invariably tended to produce deep pitting as well as rapid corrosion of the edges of the deposits. Alcoholic solutions were found to yield the most promising results. Of these solutions, the best was one consisting of 50 c.c. of ethyl alcohol saturated with dimethyl glyoxime and containing from 1 to 1·5 c.c. of dilute hydrochloric acid (10 c.c. of concentrated hydrochloric acid in 90 c.c. of water). This is the etching solution which is now being employed in this laboratory. It has given consistently good results and is capable of producing a uniform and easily controllable etch.

When nickel is made anodic in this solution, the nickel chloride formed is immediately precipitated as nickel dimethyl glyoxime. Though the alcohol need not be saturated with dimethyl glyoxime, the amount present should be sufficient to cause the precipitate to form directly on the surface of the corroding nickel. Uniform etching and absence of pitting appear to result from a protective action exerted by a coating of insoluble, yet loosely adherent, nickel dimethyl glyoxime at those areas where the metal may tend to corrode most rapidly. Any tendency for the edges of the nickel specimen to corrode away rapidly can be entirely eliminated by depositing a layer of copper on the surface of the nickel before mounting the specimen for polishing.

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[1] Instructor in Electrochemistry, Department of Chemical Engineering, University of Wisconsin.

[2] W. A. Mudge, *Metal Progress*, Dec. 1930, p. 72.

[3] G. E. Gardam and D. J. Macnaughton, *Trans. Faraday Soc.*, 1933, **29**, 755.

[4] W. Blum and C. Kasper, *ibid.*, 1935, **31**, 1203.

In order to obtain good control of the etching rate, the current density must necessarily be low, though its value is not particularly critical. Good results were obtained with current values ranging from 6 to 20 milliamperes when applied to a specimen having a total surface area (nickel plus copper) of approximately 0·1 sq. cm. The time of etching depends on the current density used. A specimen may be etched for 5 or 10 seconds, cleaned, dried, and examined, and the etching process repeated until the desired effect has been obtained.

The best results were obtained when the cathode area was considerably larger than the area of the nickel to be etched. Thus, when a platinum wire was used as cathode, the resulting etch was not as uniform as that obtained when a cathode of thin sheet nickel (about 1 cm. by 10 cm.) was placed opposite and directly below the nickel specimen during the etching process. Such an arrangement permits a more uniform distribution of the current over the anode surface in this high resistance electrolyte.

The accompanying photomicrographs are representative of the results attained by this method of electrolytic etching. Before cutting out the small specimens intended for metallographic examination, the nickel deposits were first plated with copper. The specimens were then mounted in bakelite according to the method of D. E. Krause and J. F. Oesterle.[5]

Figs. 1 to 4 inclusive show the structures of nickel deposits obtained from nickel sulphate plating solutions containing different chloride salts as the anode corroding agent. The curved microstructures (Figs. 1 and 3) illustrate the types of deposits along the edges of the cathodes. The structure shown by Fig. 4 was purposely etched rather heavily in order to indicate the absence of pitting. Figs. 5 and 6 show the structures revealed when the electrolytic etching method is applied to specimens of cold drawn and annealed commercial nickel rod.

It will be observed that the copper basis metal as well as the electrodeposited copper on the outer surface of the nickel is not appreciably attacked when the nickel is electrolytically etched. Furthermore, the edges of the deposits can be made to show a sharp line of demarcation between the nickel and the copper. A broad line of demarcation between these two metals, as seen in Fig. 3, generally results from a slight rounding of the nickel surface if the process of etching and repolishing on the final cloth covered wheel is repeated several times.

Perhaps the most annoying disadvantage inherent in the electrolytic method is that very slight scratches on the polished metal surface tend to become more pronounced by the etching process. Generally, such scratches can be almost entirely eliminated by careful repolishing on the final wheel after giving the specimen a light preliminary etch.

Summary.

An electrolytic etching method is presented whereby the microstructure of relatively thin deposits of electrolytic nickel may be revealed. By this method, pitting and a rapid attack of the edges of the deposit are avoided. When the nickel is deposited on copper, no attack of the basis metal takes place.

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[5] D. E. Krause and J. F. Oesterle, *Metal Progress*, Nov. 1933, p. 33.

ON HIGH DIELECTRIC CONSTANTS.

By F. C. Frank.

Received 16th December, 1936.

Chemical Constitution and Dielectric Constant.

The equation of Clausius, Mosotti, Lorenz and Lorentz makes allowance for the mutual effect of the induced electric doublets in a material dielectrically polarised by the application, from without, of an electric field. This equation is precise in some conditions and is, in general, a good approximation, subject to minor corrections for assignable causes which need not immediately concern us. Subject to this allowance, the electrical polarisability of the matter in a given space is additive in terms of the quantity

$$p = \sum \frac{P_1}{V_1} = \frac{\epsilon - 1}{\epsilon + 2}, \quad . \quad . \quad . \quad . \quad (1)$$

where ϵ is the dielectric constant, p the *volume polarisation*, P_1 the *molar polarisation*, and V_1 the molar volume, *i.e.* the space containing 1 gram molecule of each molecular species present. This applies not only for the sum of the contributions of the components of a mixture, but also for the contributions of a single substance classified under the heads electronic, atomic and orientation polarisation. On the other hand, in electrical practice the dielectric constant is the important quantity. Rewriting (1)

$$\epsilon = \frac{3}{1 - p} - 2, \quad . \quad . \quad . \quad . \quad (2)$$

we see that ϵ increases very rapidly with increase of p when p approaches 1, *i.e.* when ϵ itself is large. This is illustrated by the following examples:

$\epsilon = 4$, $p = 0.5$; increase of p by 0·01 raises ϵ by 0·12.
$\epsilon = 100$, $p = 0.97$; „ „ p „ 0·01 „ ϵ „ 53.

Hence incidentally, ϵ, when large, becomes very sensitive to changes of temperature, purity, or anything which can affect p, for

$$\frac{d\epsilon}{dp} = \frac{3}{(1 - p)^2} = \frac{(\epsilon + 2)^2}{3}. \quad . \quad . \quad . \quad (3)$$

The electric displacements in matter are classified as electronic, atomic, and orientation polarisations (p_e, p_a, p_o). The first is due to displacement of electrons only, essentially the "valency electrons" of the matter present. This displacement occurs at visible and all lower frequencies. If n is the refractive index (strictly speaking, with optical dispersion eliminated by an extrapolation formula),

$$p_e = \frac{n^2 - 1}{n^2 + 2}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The other two contributions involve displacement of atomic nuclei, which only commences at infra-red frequencies. For such displacements to have a dielectric effect, the atoms must carry a net electric charge: *i.e.* they must be ions or form part of polar linkages. When the restoring force opposing this displacement is elastic in nature, the polarisation produced is mainly independent of temperature and is called *atomic polarisation.* When the restoration is brought about thermally, by the randomising effect of Brownian motion, the resulting polarisation is inversely proportional to the absolute temperature; this normally arises in practice by the orientation of molecules with permanent electrostatic dipoles, and is called *orientation polarisation.* The equation for the polarisation now becomes

$$\begin{aligned} p &= p_e + p_a + p \\ &= \frac{4\pi n}{3}\left(\alpha_e + \alpha_a + \frac{\mu^2}{3kT}\right), \qquad . \quad . \quad . \quad (5) \end{aligned}$$

for a single molecular species. Here $n(=N/V)$ is the number of molecules in unit volume, α the polarisability of a molecule (subscripts indicating whether it refers to electronic or atomic polarisations), μ the molecular dipole moment, k Boltzmann's constant $1 \cdot 37 \times 10^{-16}$, T the absolute temperature.

From an elementary application of this formula, it appears easy to obtain an infinite dielectric constant from orientation polarisation; *e.g.*, nitrobenzene with a dipole moment of 4×10^{-18} e.s.u. would be expected to give an infinite dielectric constant by orientation alone at a concentration of 0·37 gm./c.c. Yet in fact, the D.E.C. of the pure liquid (density, 1·20 gm./c.c.) is only 35. This is because interactions between dipole molecules cause another force opposing orientation in addition to that provided by thermal agitation. This effect of all the rest of the dipoles upon each is approximately measured by the dielectric constant they produce:[1, 2, 3] hence this interaction keeps pace with the increasing dielectric constant and prevents it from ever reaching an infinite value. The largest values will be obtained when the dipole is near to the centre of a nearly spherical molecule (*e.g.*, liquid HCN and liquid HF which reach values of 194 and 175).

This applies to a fairly uniform random distribution of dipoles, as in a liquid. When in a crystal, other forces hold their centres in special positions, the interactions are not necessarily negative but may become co-operative: *e.g.*, Rochelle salt, in which ϵ along one axis approaches ∞ at certain temperatures, values up to 15,000 having been measured.[4, 5, 6]

There is a large range of liquids with high dielectric constants owing to orientation polarisation, going up to about 90, with a few even higher such as those mentioned above. Solids with high dielectric constants owing to dipoles are unusual and rather impractical. Such are: at low temperatures, the solidified halides and sulphides of hydrogen, ice, dimethyl sulphate and methyl alcohol; at room temperature ethylene cyanide (67) and certain substances containing water of crystallisation, *e.g.*, magnesium and yttrium platinocyanides (up to 330), as well as Rochelle salt. These hydrated substances are not very stable: owing to the magnifying effect of the polarisation function a substance must

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[1] R. P. Bell, *Trans. Faraday Soc.*, 1935, **31**, 1557.

[2] P. Debye, *Physik. Z.*, 1935, **36**, 100.

[3] Arkel and Snoek, *Trans. Faraday Soc.*, 1934, **30**, 707.

[4] R. H. Fowler, *Proc. Roy. Soc.*, *A*, 1935, 149.

[5] Frenkel, Todes and Ismailow, *Acta Physochimica U.S.S.R.*, 1934, **1**, 97.

[6] Kurtschatow, *Physik. Z. Sow.*, 1933, **3**, 304, 321.

TABLE I.*

Ion.	α.	r.	r^3.	α/r^3.
Inert Gas Structure Ions.				
He	0·197	—	—	—
Li^+	0·079	0·78	0·475	0·166
Be^{2+}	0·035	0·34	0·039	0·891
B^{3+}	0·020	(0·26)†	(0·018)	(1·14)
C^{4+}	0·012	0·20	0·008	1·5
O^{2-}	2·76	1·32	2·30	1·20
F^-	0·985	1·33	2·36	0·417
Ne	0·394	—	—	—
Na^+	0·197	0·98	0·94	0·210
Mg^{2+}	0·114	0·78	0·475	0·240
Al^{3+}	0·067	0·57	0·186	0·360
Si^{4+}	0·039	0·39	0·059	0·657
S^{2-}	5·90	1·74	5·27	1·12
Cl^-	3·43	1·81	5·93	0·579
A	1·65	—	—	—
K^+	0·879	1·33	2·30	0·382
Ca^{2+}	0·531	1·06	1·19	0·444
Sc^{3+}	0·382	0·80	0·51	0·75
Ti^{4+}	0·272	0·64	0·262	1·04
Se^{2-}	6·42	1·91	6·96	0·922
Br^-	4·80	1·96	7·53	0·638
Kr	2·51	—	—	—
Rb^+	1·81	1·49	3·31	0·547
Sr^{2+}	1·42	1·27	2·05	0·692
Y^{3+}	1·02	1·06	1·19	0·857
Zr^{4+}	0·800	0·87	0·66	1·21
Te^{2-}	9·60	2·11	9·40	1·02
I^-	9·29	2·20	10·64	0·684
X	4·10	—	—	—
Cs^+	2·48	1·65	4·49	0·552
Ba^{2+}	1·69	1·43	2·92	0·579
La^{3+}	1·58	1·22	1·82	0·869
Ce^{4+}	1·20	1·02	1·06	1·13
Pseudo-inert Gas Structure Ions.				
Cu^+	1·81	1·0	1·0	1·81
Zn^{2+}	0·114	0·83	0·572	0·199
Ag^+	1·85	1·13	1·44	1·28
Cd^{2+}	0·96	1·03	1·09	0·88
Hg^{2+}	1·99	1·12	1·41	1·41
Other Ions.				
Cu^{2+}	0·670	(0·82) †	(0·552)	(1·21)
Pb^{2+}	4·34	1·32	2·30	1·89

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* Values of α are mainly calculated from ion refractivities quoted by Smyth (*Diel. Const. and Mol. Struct.*, p. 148), but with some reference to Born and Heisenberg's figures. Values for Cu, Ag, Hg and Pb are taken from the refractivities of cubical crystals, and may be less accurate than the rest. Radii are nearly all Goldschmidt's values, as tabulated in Sidgwick's "Covalent Link in Chemistry."

† Interpolated.

be very stable to show a steady reproducible high D.E.C. They also show dispersion and absorption in the radio range, and in addition Rochelle salt at room temperature shows hysteresis and strong variation of the dielectric " constant " with field strength and temperature. This class is a bad one among which to look for practical materials of high D.E.C.

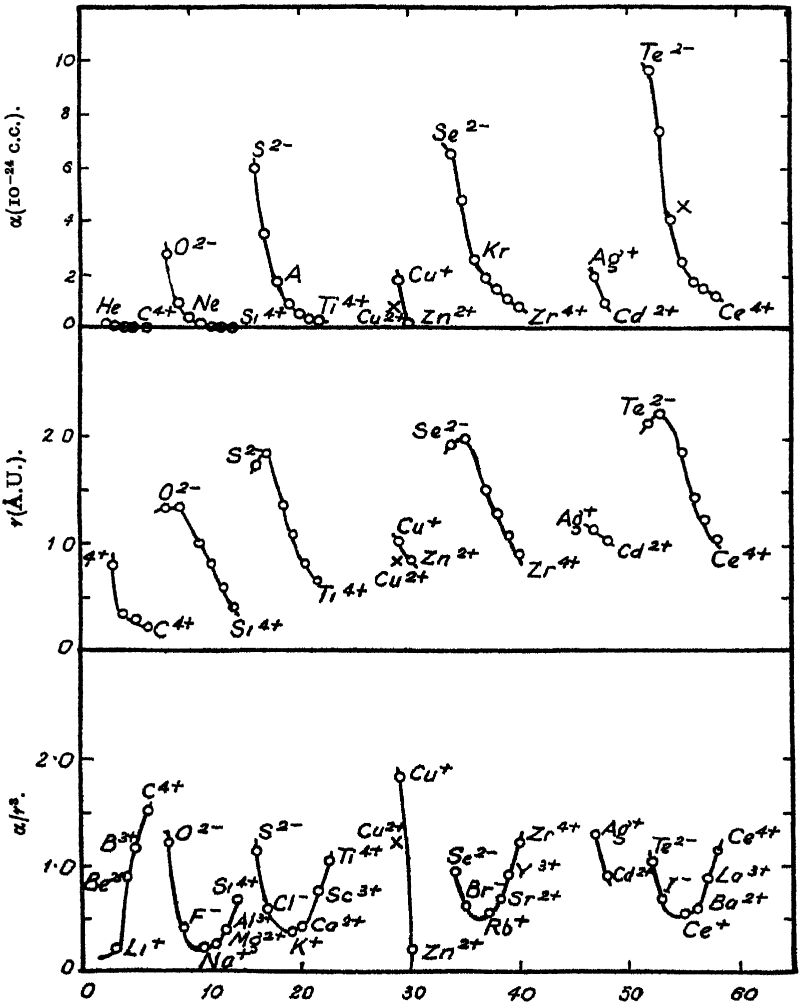

Fig 1.

Though electronic and atomic polarisations separately are incapable of giving values of p approaching 1 and hence high values of ϵ, they can do so together when both are high. To a fair approximation the *electronic polarisation* or refractivity of a substance is the sum of the refractivities of its constituent atoms or ions. Thus, the greatest value of p_e will be obtained by bringing the largest possible number of the most polarisable atoms or ions into a given space. Therefore we must seek atoms or ions having the largest values of α/r^3, α being the polarisability of the atom or ion, r its radius. Table I. and the accompanying graphs show values of α, r^3 and their ratio for a number of ions; α would be equal to r^3 if the ions were conducting spheres.

We must have large values of α/r^3 to obtain large values of p_e. Of those quoted in the table, the following have $\alpha/r^3 > 1$: B^{3+}, C^{4+}, O^{2-}, S^{2-}, Ti^{4+}, Cu^{+}, Cu^{2+}, Zr^{4+}, Ag^{+}, Te^{2-}, Ce^{4+}, Hg^{2+}, Pb^{2+}. Particularly low values are given by Zn^{2+} and the alkali and alkaline-earth metals. It follows that the latter must not be large constituents of a substance which is to have high D.E.C. It should be noticed that anions have much larger volumes and refractivities than cations, and are therefore more important than the latter. We are restricted to oxides, sulphides and tellurides among the simple anions, the last being rare. We can also provide a high concentration of oxygen by introducing complex ions (nitrates, carbonates, silicates, etc.), but in most of these the refraction of the oxygen is reduced to about half its value as a free ion. The reduction is least when the central " ion " of the complex is fairly large, and is only slight in the case of the titanates [7] (it is only as a convenient fiction that we refer to such ions as C^{4+} which are really covalently combined; but in the titanates the binding must be much more fully ionic).

Most of the ions quoted in the table are of inert gas structure. Among these it is clear that the highest values of α/r^3 are given by ions of highest charge, both positive and negative.

A number of ions are not included in Table I. The hydrogen ion has no free permanent existence, being always covalently combined. If we assign values to a fictitious free H^+, we must give it a somewhat variable negative α, but usually a positive r, so that hydrogen-containing compounds will not in general have large values of p_e. The other important omissions are the " transition elements," V, Cr, Mn, Fe, Co, Ni, and their relatively rare higher homologues, together with some ions of " pseudo inert gas " structure, a few of which (Cu, Ag, Zn, Cd, Hg) are quoted. Both classes probably give fairly large values of α/r^3, but measurement of the ionic refractions of the former is complicated by their colour. Tl^+ is a particularly unfortunate omission since several of its compounds have high dielectric constants. Cu^+, which shows a particularly high value, is unstable in most of its compounds, oxidising to Cu^{++}. Many of the oxides and sulphides of metals in these two classes are semi-conductors.

Table II. gives a list of inorganic solids mentioned in I.C.T. with $\epsilon > 13$, and shows clearly that all contain constituents with high α/r^3:—

TABLE II.

PbO	26	$TlCl$	47	SnO_2	24
PbS	18	$TlBr$	54	$HgCl_2$	14
$PbSO_4$	14	CuO	18	$PbMoO_4$	24
$Pb(NO_3)_2$	17	FeO	14	$Pb_5Cl(PO_4)_3$	47·5
$PbCO_3$	24	TiO_2	114		

A list of substances with high refractive indices brings out the result even more clearly. The following in I.C.T. have $n_D > 2{\cdot}5$: Cu_2O,

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[7] C. P. Smyth, *Dielectric Constant and Molecular Structure*, 1931, p. 159.

PbS, CdS, TiO_2, $CaFe_2O_4$, SiC, HgS, $Ag_6As_2S_6$, HgO, $HgSb_4S_7$, $Ag_6Sb_2S_6$, $Ag_{16}Sb_2S_{11}$, Sb_2S_3. Most of these have been shown to be semi-conductors.

In fully ionic substances *atomic polarisation* can be quite a large fraction of the whole : e.g., in NaCl it is equal to the electron polarisation, and in all the alkali metal fluorides it is larger.[8]

Atomic polarisation arises by motion of the positive ions of the lattice relative to the negative ions. The ease of this lattice distortion rests ultimately on the ease of distortion of the ions, chiefly the anions. The dielectric effectiveness of the distortion depends on the charge carried by the ions. TiO_2 eminently satisfies the criteria for high p_a, having easily distorted oxygen anions and quadruply charged cations. Compounds of Pb^{2+} or Tl^+ which have as high (or higher) p_e values as titanium compounds, fail to reach such high D.E.C. as TiO_2 because their smaller ionic charges produce smaller p_a.

Crystal structure is important in two ways : firstly, density. The closest possible packing is necessary if a substance is to have a high D.E.C. A given crystal structure is only the closest packing for a particular ratio of the radii of the ions ; *e.g.*, the NaCl structure is a very close packing when one set of ions is small and fits into the interstices between the other set of large ions. LiCl, or better still LiBr ($\epsilon = 12·1$), is a good example of this. Table III. illustrates the effect.

TABLE III.

	LiCl.	NaCl.	KCl.	RbCl.
P . .	15·80	16·68	20·83	25·21
ϵ . .	11·05	5·77	4·76	5·20

The molecular polarisations rise steadily, but the D.E.C.'s fall and pass through a minimum. In the same way a polymorphic substance has highest ϵ in its densest form : *e.g.*, TiO_2 (Table IV.) :
Startlingly large as the difference between these D.E.C.'s appears, it is actually less than corresponds to the change in density ; calculating from ϵ_{mean}, the molar polarisation is greatest in anatase. This change is mainly in the atom polarisation, p_e (not extrapolated) being approximately 13 c.c. in each case, though slightly highest in anatase.

TABLE IV.

	Rutile.	Brookite.	Anatase.
Density .	4·21	4·11	3·87
ϵ_{mean} .	114	78	48
P . .	18·5	18·7	19·4

The other effect of crystal structure is in certain cases to produce large differences of ϵ along different crystal axes (this is exceedingly pronounced in the hydrated crystals which show orientation polarisation) ; *e.g.*, for rutile it is 173 and for pyromorphite ($\epsilon_{mean} = 47·5$) 90·5 along the principle axis. These are, of course, relatively small differences when expressed as polarisations. Part of the explanation is as follows :[9] In a "unidimensional crystal" (Fig. 2*a*), polarisation along the chain two oppose, but the first two pull twice as strongly. In both 2*a* and 2*b* the polarisability is correspondingly reduced in a direction at right angles to the line or plane. In a cubical crystal the co-operative effect of the neighbours becomes zero, for now four neighbours oppose, and two assist twice as strongly. In this case we have the Clausius-Mosotti conditions. When the crystal is not cubical, but contains line or layer structures, it may be expected to show excess polarisation along the line or layer and reduced polarisation across it; *e.g.*, in the crystal structure of rutile all the ion centres are contained in two intersecting sets of parallel planes, the distance between which is about 5/3-times the distance between neighbours within a plane. Both sets of planes contain the principle axis along which the dielectric constant is maximum.

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[8] Errera, *Z. Elektrochem.*, 1930, **36**, 818.

[9] *Cf.* W. L. Bragg, *Proc. Roy. Soc.*, *A*, 1924, **105**, 370.

What we have just said applies to the electronic polarisation of ions or atoms whose positions are fixed. The array affects differently the ionic polarisation dependent upon their displacement. In general, similar ions move together, so that their mutual effects are unaltered tends to be co-operative; the field of each induced dipole tends to induce dipoles in the same direction in its neighbours. In a "two-dimensional crystal" (Fig. 2*b*) the same is true: two neighbours assist, by the displacement and their relative situations are unimportant. It is the relative situation of unlike ions that is important in this case.

It would seem to be necessary to make a specific study of the lattice vibrations in each crystal type in order to give a complete account of the directional properties of ionic polarisation, but we may state as a semi-empirical rule that ionic polarisation is largest in the directions in which ions of opposite charge alternate. This bears chiefly upon crystals containing alternately layers of positive and negative ions. Ionic polarisation is greatest perpendicular to these layers, whereas in accordance with the principles of the preceding paragraph electronic polarisation is greatest parallel to the layers.

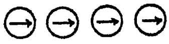
FIG. 2*a*.

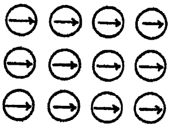
FIG. 2*b*.

This is exemplified most clearly by the rhombohedral and orthorhombic carbonates (Table V.). In these, the planar carbonate ions lie flat in densely packed layers with cations in intermediate planes. These planes are parallel to the *a* and *b* axes. It is clearly seen that p_e is greatest in the planes and p_a greatest perpendicular to them. We have no layer lattice in the orthorhombic sulphates: the electronic polarisation is fairly isotropic but the dielectric constant is enhanced along one axis, apparently owing to anisotropy in the lattice vibrations.

The figures in Table V. were taken or calculated from those given by Errera and Brasseur.[10] These authors showed that the ionic polarisations concerned were due to lattice vibrations, not to internal vibrations of the SO_4^{2-} or CO_6^{2-} ions, from the position in the infra-red spectrum at which the anisotropy began to appear (the former vibrations have frequencies around 4×10^{13}, the latter around 4×10^{12}). They were of the opinion that anisotropy of dielectric constant is almost entirely due to ionic polarisation. This chances to be true in the sulphates, but in the carbonates (excepting magnesite) anisotropy of p_e dominates throughout, and is of the same magnitude as the anisotropy of p_a in the sulphates. Of course, owing to the "accelerating" nature of ϵ as a function of p, the ionic component entering on passing through the infra-red range makes the differences startlingly apparent.*

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[10] J. Errera and H. Brasseur, *Physik. Z.*, 1933, 34, 369.

TABLE V.

	n_D.			ϵ.			p.			p_ϵ.			p_a.		
	a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
Rhombohedral Carbonates.*															
$MgCO_3$ Magnesite	1·717		1·528	6·91		8·1	0·663		0·703	0·394		0·308	0·269		0·395
$CaCO_3$ Calcite	1·658		1·486	8·5		7·56	0·715		0·686	0·377		0·287	0·338		0·399
$CaMg(CO_3)_2$ Dolomite	1·692		1·506	7·80		6·80	0·694		0·659	0·382		0·296	0·312		0·363
$MnCO_3$ Rhodochrosite	1·814		1·597	8·22		7·09	0·706		0·670	0·433		0·340	0·273		0·330
$FeCO_3$ Siderite	1·872		1·631	7·9		6·9	0·697		0·664	0·455		0·356	0·242		0·308
$ZnCO_3$ Smithsonite	1·882		1·612	9·4		9·3	0·736		0·735	0·459		0·348	0·277		0·38
Orthorhombic Carbonates.															
$CaCO_3$ Aragonite	1·681	1·685	1·530	12·82	8·09	6·64	0·797	0·702	0·652	0·378	0·380	0·309	0·419	0·322	0·343
$SrCO_3$ Strontianite	1·666	1·668	1·520	7·69	7·56	6·58	0·690	0·686	0·650	0·371	0·372	0·304	0·319	0·314	0·346
$BaCO_3$ Witherite	1·676	1·677	1·529	7·8	7·5	6·35	0·694	0·685	0·640	0·376	0·376	0·309	0·318	0·309	0·331
$PbCO_3$ Cerusite	2·074	2·076	1·802	25·4	23·2	19·2	0·890	0·881	0·858	0·524	0·524	0·429	0·366	0·357	0·429
Orthorhombic Sulphates.															
$SrSO_4$ Coelestine	1·631	1·623	0·622	7·7	18·5	8·3	0·691	0·854	0·709	0·356	0·353	0·352	0·335	0·501	0·357
$BaSO_4$ Barite	1·648	1·637	1·636	7·65	12·6	7·7	0·689	0·795	0·691	0·363	0·359	0·358	0·326	0·436	0·333
$PbSO_4$ Anglesite	1·895	1·883	1·878	27·5	54·6	27·3	0·898	0·947	0·898	0·463	0·459	0·457	0·435	0·488	0·441

On the Temperature Coefficient of Dielectric Constant.

A minimal temperature coefficient of dielectric constant is generally desired in practical dielectrics. Substances of high dielectric constant are liable to have high temperature coefficients, for from equation (3) it is seen that for a given temperature coefficient of p the temperature coefficient of ϵ, $\left(\frac{1}{\epsilon} \cdot \frac{d\epsilon}{dT}\right)$ is proportional to $(\epsilon + 2)^2/\epsilon$. It is therefore more than usually necessary in this case to examine the causes of temperature dependence of dielectric constant and to decide in what circumstances it will be least.

Temperature change may alter both the density and the restoring forces which oppose electric displacement. The variation due to change of density alone is given by

$$\frac{1}{\epsilon}\left(\frac{\partial\epsilon}{\partial T}\right)_p = -\frac{1}{3}(\epsilon - 1)(\epsilon + 2)\,\frac{1}{V}\left(\frac{\partial V}{\partial T}\right). \qquad . \quad . \quad (6)$$

The change of electronic polarisation with temperature is almost negligible, so that when most of the polarisation of a material is electronic the variation of ϵ with T is given to a good approximation by this equation.[11]

Orientation polarisation is inversely proportional to the absolute temperature in simple cases, so that when this is present the temperature dependence is usually very great. In the extreme case of a substance whose polarisation is all due to orientation, the temperature coefficient will be

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* Errera and Brasseur tabulated and discussed the fraction $(\epsilon - n_0^2)/(\epsilon - 1)$ as a measure of ionic polarisation. This has no special advantage, but sacrifices directness of physical interpretation and ease of comparison with other dielectric studies.

[11] *Cf.* E. Bretscher, *Trans. Faraday Soc.*, 1934, 749.

$$\frac{1}{\epsilon}\left(\frac{\partial\epsilon}{\partial T}\right)_V = -\frac{(\epsilon+1)(\epsilon+2)}{3\epsilon T}. \quad . \quad . \quad . \quad (7)$$

As was explained above, however, this value will be a limit which is not reached when ϵ is high, since by mutual interactions the neighbouring molecules of a dipole produce an extra restoring force which is not of thermal origin. Moreover, this effect is reduced by increase of temperature so that in exceptional cases the dielectric constant actually increases even where it is largely due to orientation (*e.g.*, acetic acid, secondary and tertiary octyl alcohols).[12] Usually, however, a high dielectric constant due to orientation falls very rapidly against temperature, *e.g.*, liquid HCN (Table VI.)

TABLE VI.

Temp.	
$-13\cdot4°$	194·4
$+1\cdot1°$	149·8
$+20\cdot0°$	116·1

Unlike electronic and orientation polarisation, atomic polarisation increases with temperature owing to the loosening of the crystal, which allows a given electric field to produce a greater displacement of ions. A simple method of calculating this has been given by Bretscher,[13] and a more complicated but more precise method by Blackman,[14] the result being in fair agreement with measured temperature coefficients. In the cases of NaCl and CaF_2 to which it has been applied, this effect is of the same order as, but larger than, the effect of density change which works in the opposite direction; the final temperature coefficient being the difference of these is therefore positive (Table VII.).

TABLE VII.—TEMPERATURE COEFFICIENT OF ϵ.

	$\frac{1}{V}\frac{\partial V}{\partial T}$.	Coeff. Due to Density Change.	Coeff. Due to Loosening of Crystal.	Difference.	Experimental Coeff.
NaCl	$1\cdot21\times10^{-4}$	$-1\cdot11\times10^{-4}$	$+3\cdot23\times10^{-4}$	$+2\cdot12\times10^{-4}$ $3\cdot27\times10^{-4}$ (Blackman)	$+3\cdot8\times10^{-4}$
CaF_2	$0\cdot57\times10^{-4}$	$-0\cdot57\times10^{-4}$	$+1\cdot37\times10^{-4}$	$+0\cdot87\times10^{-4}$	$+2\cdot5\times10^{-4}$

It is probable that in other substances it may be close to zero, since in covalently linked substances it is negative, being fairly accurately given by equation (7). Such substances are likely to be those with lower ratios of p_a to p_e (this ratio is about 1 in NaCl). It ought, therefore, to be possible by choice of composition to make ceramics having zero or any desired temperature coefficient of dielectric constant, though perhaps not together with the highest possible value of dielectric constant. A particularly convenient temperature coefficient would be equal and opposite to the temperature coefficient of linear expansion.

Where there are large differences of dielectric constant along different crystal axes, these differences are likely to diminish against temperature as neighbouring ions move further away from each other. A high dielectric constant along a single axis will probably, therefore, have a rather large negative temperature coefficient.

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[12] C. P. Smyth and H. E. Rogers, *J. Amer. Chem. Soc.*, 1930, **52**, 1826.

[13] E. Bretscher, *Trans. Faraday Soc.*, 1934, **30**, 684.

[14] M. Blackman, *ibid.*, 1935, **31**, 545.

So far we have only considered the temperature coefficient of perfect dielectrics, free from dielectric loss. All recognised mechanisms of loss necessarily imply simultaneous anomalous dispersion. This will be reflected in the variation of ϵ with temperature, because the characteristic relaxation time τ of the loss-and-dispersion mechanism generally decreases rapidly against temperature. As a result of this, a finite dielectric loss implies therewith a positive contribution to the temperature coefficient of dielectric constant, which is quite large in the neighbourhood of a maximum of dielectric loss, but small elsewhere.

In glassy materials there is usually no pronounced maximum of loss either against temperature or frequency, and the contribution of the thermal dispersion effect must be small. Nevertheless, there is often a considerable rise of dielectric constant with temperature which must be attributed to the release into a state permitting rotation of gradually increasing numbers of polar groups of atoms. In crystalline substances generally this only occurs abruptly at a definite temperature (*e.g.*, camphor or solid HCl).

High Dielectric Constant and Electronic Semi-Conduction.

If a list of materials exhibiting electronic semi-conduction is examined, it will be found to show a striking similarity to a list of substances of high dielectric constant drawn up in accordance with our criteria. The following list of substances mentioned in Gudden's article [15] on the subject of electronic semi-conduction illustrates the point: α-Ag_2S, Cu_2O, cuprous halides, NiO, UO_2, ZnO, CdO, CuO, Wo_3, Cr_2O_3, CdS, CoO, TiO_2, V_2O_5, PbO_2, Bi_2O_3, MnO_2, CuS, PbS, Co_3O_4, MnO, PbO, ReO_2, RuO_2, SnO_2, Tl_2O_3, U_3O_8, SnO, Tl_2O, and possibly Ag_3SbS_3, Ag_3AsS_3, $AgSbS_2$, CuS_2. This correlation is not unexpected, for we can anticipate a close correlation between the ease of removal of an electron from an ion and the distortibility of the electronic shell of that ion. Moreover, the stability of the free electron and the anomalously-charged ion which it leaves will presumably be greater in a medium of higher dielectric constant. The correlation observed is also to be expected from another point of view, for there is a clear connection between semi-conduction and photoconduction, which Gudden [16] has already shown to be a characteristic property of substances with refractive index > 2. The conductivity is a very erratic property, and may vary bya fact or of 10^6 or more from sample to sample of the same semi-conductor, being enormously sensitive to minute amounts of impurity as well as to physical treatment. The photo-conductivity on the other hand is a much more consistent property. The current explanation is that a photon raises normally-placed electrons into a mobile state, whereas thermal fluctuation energies which are responsible for conduction in the dark are only adequate to release electrons which already have abnormally high potential energy. These may occur at positions of lattice distortion, or where foreign ions are present. The conditions of semi-conduction, therefore, are twofold: (*a*) the substance must be capable of becoming a semi-conductor, given the right sort of imperfections; and (*b*) the right sort of imperfections must be present. Conditions (*a*) will be much the same as for photoconduction, and will be satisfied by all substances with high electronic volume polarisation, possibly by all with high dielectric constant. It is in condition (*b*) that we have the chance of controlling conductivity. Here we may be guided by the Friederich-Mayer rule:

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[15] *Ergebnisse der Exakten Naturwissenschafter,* 1934, **13.**

[16] *Ergebnisse,* 1924, **3.**

"In unsaturated compounds of lowest valency level conductivity increases with non-metal excess (*e.g.*, CuI, Cu_2O, NiO, CoO, VO_2). In saturated compounds it increases with non-metal deficiency (*e.g.*, WO_3, ZnO, CdO, TiO_2)."

Exceptions to the rule are the highly conducting substances V_2O_5, PbO_2, Bi_2O_3, MnO_2, where we probably have interfering boundaries, as in CuS and PbS. The two latter are best classed with the metals.

Le Blanc and Sachse's conclusions, which are closely related to Meyer's rule, show that the intermediate compounds of a series of variable valency will generally be poor insulators.

Meyer's rule, applied to rutile, indicates that it must be fully oxidised up to the state of TiO_2 in order to minimise conduction, but an excess of oxygen will not be harmful. On the other hand very slight reduction, almost imperceptible by chemical analysis, and quite insufficient for any formation of metallically conducting bridges, will ruin it as an insulator.

Acknowledgement is due to the Department of Scientific and Industrial Research for a grant.

Summary.

The principal effects of chemical constitution upon dielectric properties are discussed in an attempt to attain an understanding of the causes determining the dielectric constants of materials, and especially the outstandingly large values found for certain substances. It is pointed out that the Clausius-Mosotti-Lorenz-Lorentz relation, which is taken as basic, automatically leads to very great disparity among the materials of largest dielectric constant, so that the occurrence of a few materials with dielectric constants greater than 100, while the vast majority are less than 10, is less in need of special explanation than might at first appear.

It is shown that, among substances which are ionised or considerable as composed of ions, the chief criterion of high dielectric constant is a high ratio of ionic refraction to ionic volume: available measured quantities which can be used as a first guide. The effect of atomic array is the chief of the other determining factors which is dealt with.

Attention is also given to the temperature coefficient of dielectric constant and the incidence of electronic semiconduction, which chiefly limits the usefulness of many solids of high dielectric constant, as electrolytic conduction limits that of liquids.

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Oxford.

A NEW APPARATUS FOR ELECTROPHORETIC ANALYSIS OF COLLOIDAL MIXTURES.

By Arne Tiselius.

Received 25th January, 1937.

In the course of earlier work[1] on the electrophoretic migration of proteins in various buffer solutions (using a photographic-microphotometric method to follow the migration), a detailed study was made of the different sources of error in electrophoretic measurements and the possibilities of their elimination. Special interest was devoted to the electrophoretic behaviour of mixtures of proteins. It was found that the individual components in such mixtures do not usually mutually influence migration to any great extent, so that a partial separation is brought about by the current. From this we can derive conclusions as to the electrochemical homogeneity of a given colloidal solution, similar to those Svedberg derives from his ultracentrifuge molecular weight analysis. The importance of using physical methods for such a purpose is obvious: the usual methods of fractionation of biocolloids (which are very unstable and very sensitive towards even quite mild chemical agents), are often of doubtful value. The procedure was exemplified both on artificial and on natural mixtures, and was also used for the purification of proteins. Fig. 1 shows the apparatus used.

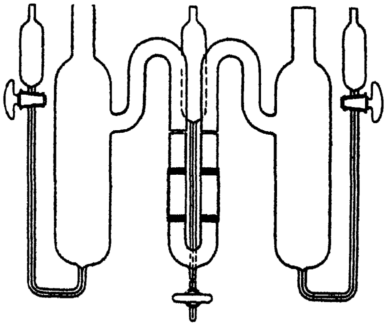

Fig. 1.—Electrophoresis apparatus for the moving boundary method (Tiselius, 1930).

The value of electrophoretic fractionation and purification of mixtures of colloidal systems was first realised by Botho Schwerin, who described an experimental arrangement and some applications of the method in a number of patents from 1914 onwards.[2] This work, of a preparative nature, was carried out in cells separated by permeable membranes. In addition to the author's work[1] on proteins, quantitative investigations (free electrophoresis with reversible electrodes) on mixtures have been carried out recently by Theorell,[3] especially on respiratory ferments, and by Bennhold[4] on the serum proteins and their reactions with other substances. Theorell also describes an apparatus with membranes and reversible electrodes for the electrophoretic purification of larger volumes of material. Electrophoretic methods provide a means of characterising the often difficultly distinguishable high molecular substances by isoelectric points and by p_H-mobility relationships, so as to get some idea of the degree of their electrochemical homogeneity, and to detect and more or less completely fractionate the homogeneous components in a mixture. It may also be possible, if suitable precautions are taken, to determine the relative proportions, and to study the degree, if any, of mutual combination of the components; in these two applications the tendency of the components to exert a mutual influence on the migration may interfere. For quantitative interpretation the experiments must be carried out at a salt concentration considerably higher than is usually needed for the depression of the boundary disturbances discussed previously.[1]

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[1] A. Tiselius, "The Moving Boundary Method of Studying the Electrophoresis of Proteins," *Inaugural Dissertation Upsala*, 1930; *Nova Acta Reg. Soc Scient. Upsaliensis*, IV., **7**, No. 4. See also, Thé Svedberg, *Trans. Faraday Soc.*, 1930, **26**, 737; and K. O. Pedersen, *Kolloid Z.*, 1933, **63**, 268.

[2] For a review of this early work see the monograph *Elektrophorese, Elektroosmose, Elektrodialyse in Flüssigkeiten*, Von P. H. Prausnitz and J. Reitstötter, Dresden u. Leipzig, 1931, especially pp. 120-122, 130, 138, 147-149.

[3] H. Theorell, *Biochem. Z.*, 1930, **223**, 93; 1934, **275**, 1, 11, 19, 30; *Naturwiss.*, 1934, **22**, 289-291; *Biochem. Z.*, 1935, **278**, 291.

[4] H. Bennhold, *Verhandl. deutsch. Ges. inn. Medizin. XLII. Kongress, Wiesbaden*, 1930, p. 353; *XLIII. Kongress, Wiesbaden*, 1931, p. 211; *Ergeb. inn. Medizin und Kinderheilkunde*, 1932, **42**, 275; *Kolloid. Z.*, 1933, **62**, 129.

The migration in the electrophoresis tube may suitably be followed by optical observation of the boundaries, or by analytical determination of the change of the quantities of the components above and below fixed levels in the tube, as used extensively for biocolloids by Hardy, Michaelis, Landsteiner and Pauli, and later by Reiner, Engel and Pauli, and Theorell.[5] Both methods have their advantages. Optical observation is particularly useful when the differently migrating substances have a similar chemical composition (*e.g.*, mixtures of proteins) which cannot be separately determined analytically. On the other hand, the analytical method alone can be used for the study of enzymes and other materials, when a measurement of activity is the only means of determining where the substance is in the tube. The apparatus for the latter method differs mainly in the provisions for sampling.

The apparatus now to be described is adapted for simultaneous use of both methods. Whichever method is being used, the modifications in the experimental arrangement resulting from the following considerations are of importance, especially in the study of mixtures and in work in media of high conductivity, and in electrophoretic fractionation.

(1) Consider two components, A and B, with the mobilities u_A and u_B migrating in the same or in opposite directions in an electrophoresis tube of cross section area q cm.^{2}. The plus sign indicates a positive charge for u_A and u_B, and *vice versa*. If the current is i amp. and the conductivity κ ohm^{-1}, the potential gradient in the tube is $i/q\kappa$ volt/cm. and the boundaries will move with the velocities $iu_A/q\kappa$ and $iu_B/q\kappa$ cm. per sec. After a time t partial separation has taken place, so that, diffusion being neglected, the volume in c.c. on each side containing pure A or B is

$$\frac{i(u_A - u_B)tq}{q\kappa} = (u_A - u_B)\frac{it}{\kappa}.$$

Independently therefore of the dimensions of the apparatus, a given degree of separation corresponds to a certain amount of electricity sent through. It is assumed that reversible electrode tubes of some sort are used, and that the ions surrounding the electrodes have a mobility of u. When the quantity of electricity $i \times t$ is sent through, these ions similarly sweep through a volume in c.c. of $u \times \frac{it}{\kappa}$. If the volume in c.c. of colloidal solution to be separated is v_s, there must be a volume of at least $\frac{u}{u_A + u_B} \times v_s$ between the electrodes and the boundaries, otherwise the ions originally present at the electrodes would reach the boundaries. In practice the volume should be about twice as large, since diffusion also interferes. If we desire to separate, say, 10 c.c. of two components with a difference in mobility of $0{\cdot}5 \times 10^{-5}$, using reversible KCl(AgCl)Ag electrodes, the mobility of K and Cl being 65×10^{-5}, the calculated electrode vessel volume should be $\frac{65}{0{\cdot}5} \times 10 = 1300$ c.c., and that used should be about 2600 c.c. The necessity of not only using reversible electrodes but also of allowing sufficient volume between the electrodes and the boundaries has often been overlooked in the construction of electrophoresis apparatus both for the moving boundary and for the transference method.

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[5] For literature references see, for example, Pauli-Valkó, *Kolloidchemie der Eiweisskörper*, 2nd ed., Chapter 10. Dresden u. Leipzig, 1933. For Theorell's work, *loc. cit.*[3].

(2) When both substances migrate in the same direction the possibility of sufficient separation is limited by the fact that long before the desired separation has been reached, both substances have migrated out of the electrophoresis tube. This is a somewhat serious limitation, since the absolute differences in mobilities are very often much larger at p_H regions where both components have mobilities of the same sign (*e.g.* the serum proteins). Moreover, lack of solubility often prevents a choice of a p_H between the isoelectric points. For this reason we arranged for a slow and uniform movement of the solution in the electrophoresis tube at an exactly known rate and in a direction opposite to the migration, by slowly lifting a cylindrical glass tube by clockwork out of the liquid in one electrode tube during the electrophoresis. If the rate at which the tube is lifted is l cm. per hour, its cross-section area p cm.^{2}, the free surface of the liquid in each electrode tube Q cm.^{2}, and the cross-section area of the electrophoresis tube q cm.^{2} then a movement of a given level in this tube will take place, at a rate of $\frac{lpQ}{q(2Q - p)}$ cm. per hour. By suitably chosing l and p any desired rate can be obtained; even in the narrow tubes used in our apparatus a rate of several centimetres per hour did not markedly blur the boundaries in the electrophoresis tube.

For fractionation purposes, this "compensation movement" is adjusted so that the observed boundary separating two fractions obtains a suitable "apparent mobility" and consequently, at the end of the run, the column of the solution can be cut off exactly at the right place (see below).

(3) The advantage of using the highest possible potential gradient for getting good separation in the electrophoresis is obvious, since some substances show diffusion, which is appreciable when compared with the rate of electrophoretic separation brought about by the potential gradients commonly applied. However, a limit is imposed in this direction by the heat evolution, which causes thermal convection currents, gradually stirring up the contents.

This source of error has been examined in some detail[1] by sending alternating current through the apparatus instead of direct current, so that the heat effects could be studied separately. By observation of the boundaries the maximum allowable potential gradient V could be determined for given conditions. From this, and from the conductivity κ, the maximum allowable load w in watts per cubic centimetre in the electrophoresis tube could be calculated from the equation $w = V^2\kappa$. From this determination, for any given conductivity, the maximum allowable V could be calculated. For the apparatus earlier used[1] with a quartz U-tube of about 0·8 cm.^{2} cross-sectional area and with protein solutions of about 0·5 per cent. strength, a maximum load of about 0·01–0·02 watts per cubic centimetre was found.

The convection currents set up with A.C. in tubes of varying shape and size, wall-thickness and so on, were studied in order to see if this maximum

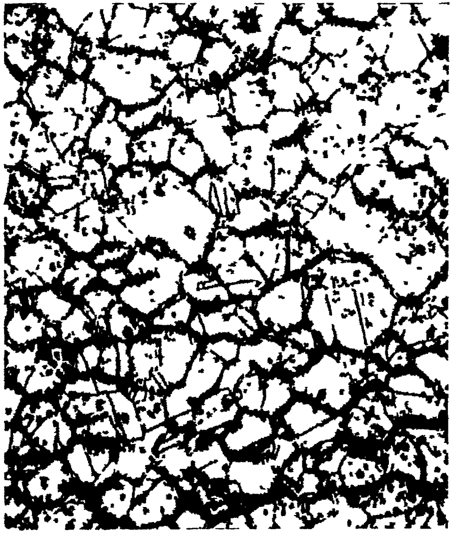

FIG. 1 —Macrocrystalline copper substrate. × 200.

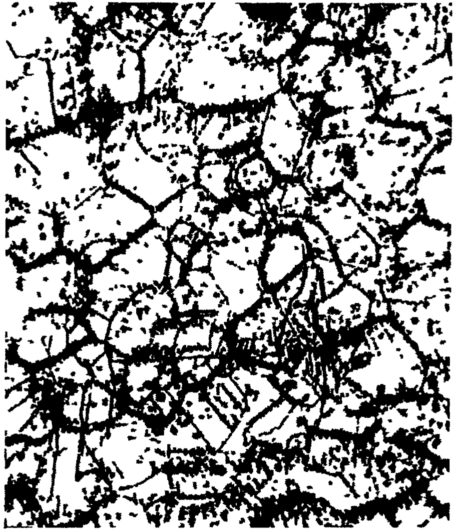

FIG 2 —Nickel deposit, 5×10^3 A thick, deposited from strong bath at 0·6 A/dcm^2 200

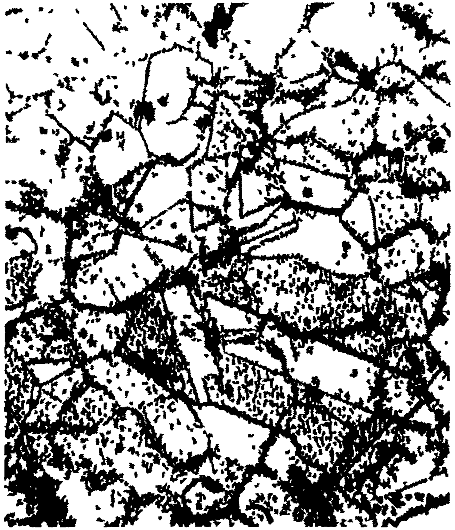

FIG 3 —Nickel deposit, 2×10^4 A thick, deposited from strong bath at 1 2 A/dcm^2 × 200

See page 567

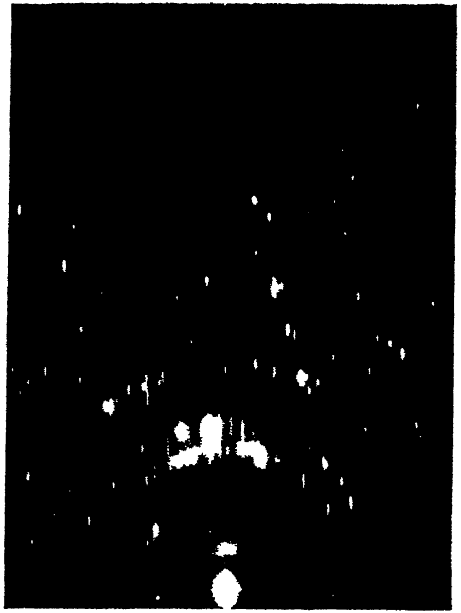

Fig 4 —Pattern from macrocrystalline copper (see Fig 1)

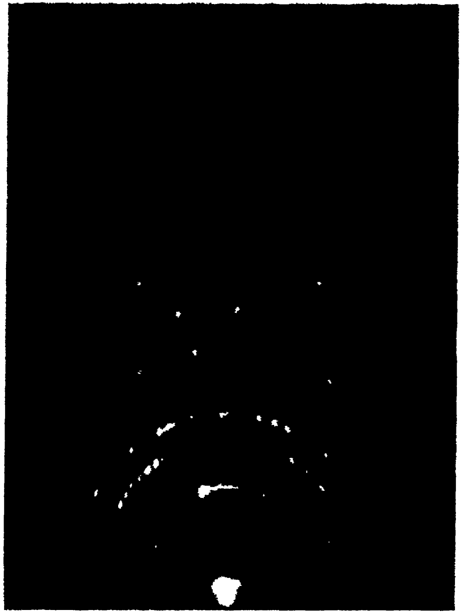

Fig 5 —Pattern from nickel deposit of Fig 2

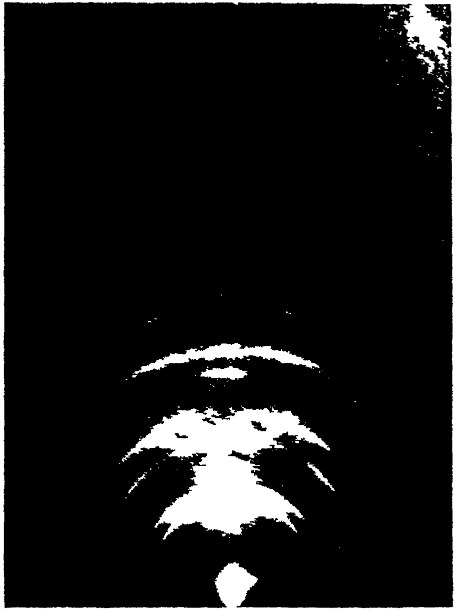

Fig 6 —Pattern from nickel deposit of Fig 3

See page 567

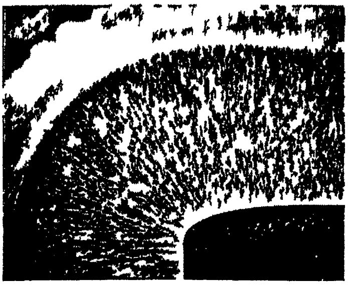

FIG 1 —Electrolytic nickel from a nickel sulphate solution containing ammonium chloride Structure along edge of cathode × 75

FIG 2 —Same deposit as Fig 1 at × 250

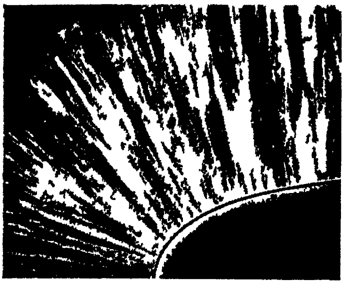

FIG 3 —Electrolytic nickel from a nickel sulphate solution containing sodium chloride Structure along edge of cathode × 75

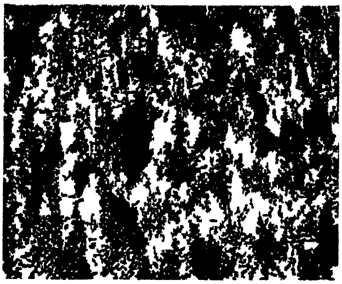

FIG 4 —Electrolytic nickel from a nickel sulphate solution containing nickel chloride × 250

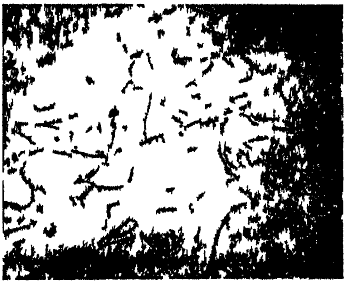

FIG 5 —Cold drawn nickel rod × 75

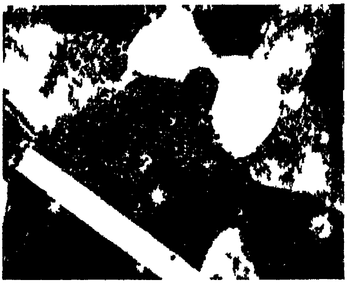

FIG 6 —Structure of nickel rod after recrystallisation × 75

[*See page* 512.

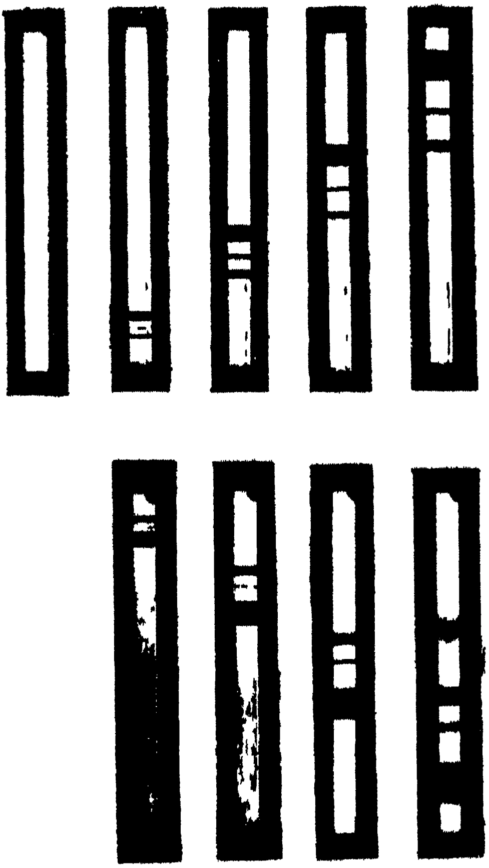

Fig. 4.—Electrophoretic analysis of blood serum. (The length of the cell is 40 mm.)

[*See page* 530.

load could be increased. Thermal convection, which invariably occurs in electrophoresis experiments at certain parts of the tube, becomes serious when the density of the central part of the solution beneath the boundary falls below that of the supernatant solution near the periphery, so that the difference in density due to the dissolved material, which keeps the boundary stable, is reduced to zero or less; at this point convection sets in, as shown in Fig. 2. However, as there is always some diffusion, layers of lower concentration above the boundary are upset by convection currents at much lower temperature differences than those at which the bulk of the solution is stirred up. This can be observed easily, when alternating current of increasing strength is sent through a U-tube with a boundary of some coloured substance.

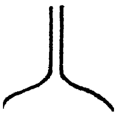

FIG. 2.—Thermal convection.

Experiment and theory both show that convection currents arise much more readily in wide than in narrow tubes. If the load is w watts/c.c., the thermal conductivity of the solution K and the temperature t, the temperature gradient $\mathrm{d}t/\mathrm{d}r$ at a distance r from the centre of a cylindrical tube is $\mathrm{d}t/\mathrm{d}r = wr/2K$, and therefore proportional to the radius. This gives for the difference in temperature between the centre and the periphery of the cylindrical column

$$t_r - t_0 = \frac{wr^2}{4K}.$$

It should therefore be very advantageous to use as narrow tubes as possible, were it not that such very small volumes of substance could then be handled. However it is possible to use *flattened* tubes: so that larger volumes can be accommodated with good heat conduction. In the apparatus to be described the electrophoresis tube has a rectangular cross-section of 3 × 25 mm., and in another apparatus under construction (for fractionating larger volumes) 5 × 100 mm. is used. With the A.C. procedure described above it was found that considerably higher load per cubic centimetre can be used than in a cylindrical tube of the same cross-sectional area; this is most marked for tubes of large cross-section.

Since thermal convection depends upon $\mathrm{d}\rho/\mathrm{d}t$, and water and the solutions usually studied have a density maximum at 4° C. or somewhat less, where $\mathrm{d}\rho/\mathrm{d}t$ is zero, it would seem that convection currents could be markedly suppressed by working at this temperature; this proved to be the case. Keeping the bath at about zero and using a load so high that the temperature in the tube is about 4° C., it was found, that, with the flattened tube, loads of 0·5-1·0 watts per cubic centimetre can very well be used; the potential gradients can therefore be about 10 times higher than before. Although the mobilities are smaller at the lower temperature, so that somewhat longer times have to be used, the diffusion being correspondingly reduced, the quality of the separation is not affected.

The advantage of using the optimum temperature was less marked for wider tubes, probably because when a large load is used, the temperature distribution of the solution is so wide that only part of the solution is at the optimum temperature.

Experimental Arrangement.

(1) The thermostat is a well insulated container taking about 100 *l* of water, and provided with double windows, between which are placed dishes with calcium chloride to prevent fog formation at the low temperature used. An Electrolux refrigeration unit of a maximum capacity of 100 kcal. per hour, but working at less than half-capacity, maintains the low temperature; the heat evolved in electrophoresis experiments usually does not exceed 20-30 kcal. per hour. Through a copper spiral wound around the evaporator of the refrigerator and connected to a similar spiral in the bath

by rubber tubing, alcohol was circulated by a small pump, driven by the same motor as the stirrer. This maintained the bath automatically at + 0·1-0·2° C., even if the cooling effect varied within very wide limits. A compact layer of ice which is formed on the spiral in the bath is not removed by the stirring; if the cooling effect is large the thickness of this layer increases, but this makes the conduction of the heat to the spiral less efficient, so that the evaporator temperature drops somewhat and the real cooling effect decreases and *vice versa*. The arrangement, providing a constant temperature just above zero, would seem useful for many laboratory purposes, for example, dialysis.

(2) The electrophoresis apparatus (Fig. 3), consisted of a central U-tube connected by thick rubber tubing with the large volume electrode vessels of which there were two pairs, one of about 2 litres capacity each for very difficult separations, the other of about 0·5 litre each. Reversible AgCl electrodes with saturated KCl solution was used as in the older apparatus, but of course the electrodes were given much larger surface. The volume of KCl in each tube was 25-100 c.c.; it was allowed to form a layer at the bottom, running down through funnel tubes shortly before starting an experiment.

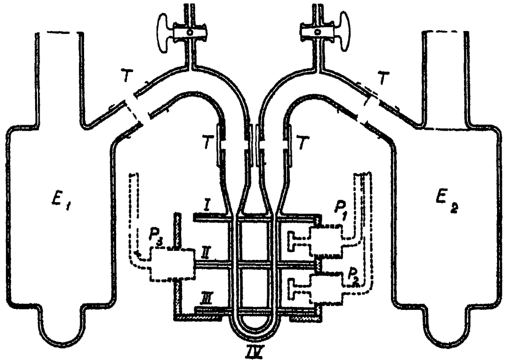

FIG. 3.—Apparatus for electrophoretic analysis. E_1, E_2 represent the electrode tubes (the larger type), T rubber tubings; I, II, III, IV, the four U-tube sections, of which II and III can be moved with the pneumatic arrangement P_1, P_2, P_3.

The U-tube, with an internal rectangular cross-section of 3 × 25 mm., was made of plain parallel glass plates, cemented together with acid-proof silicate cement; the curved walls of the U-shaped bottom part were cut from an ordinary cylindrical glass tube of the right diameter.[6]

In order to follow the migration of any number of components analytically, the contents of the U-tube must be divided into at least two portions in one limb, preferably in both limbs. In most previous constructions (Cohn, Michaelis, Landsteiner-Pauli, Reiner, Engel-Pauli), this has been done with stopcocks. Bennhold takes out samples with a capillary pipette. Theorell divides the U-tube into sections between which ebonite plates with circular holes are moved, there being as many as seven sections in each limb for isolating fractions migrating in the same direction. With the compensation device described above, no more than two sections are needed, even for this purpose. When working with high voltage, very good insulation is necessary to prevent leakage of current into the thermostat from the U-tube; our U-tube, therefore, consists of two equal sections, with one U-shaped bottom part, and one top part (for connection to the electrode tubes), all cemented to large (60 × 120 mm.) precision-ground glass plates, greased with a little vaseline thinned with paraffin oil. The arrangement resembles to a certain extent the diffusion apparatus of Cohen and Bruins.[7] The four sections are held together in a metal stand with a slight pressure by means of rubber bands, so that they may be readily moved over each other. A movement of a little over 3 mm. of one section cuts it off completely from the other. The sections are moved by the pneumatic arrangement (shown in Fig. 3 dotted lines), connected by rubber tubing to a small metal air pressure pump of the type commonly used for filling burettes, etc. This arrangement avoids vibration since necessary operations can be made without touching the apparatus. To secure exact alignment, the sections are pressed against a plane metal plate (to the right in Fig. 3). When making a run, the two lower sections are filled with the colloid, the U-tube " closed " by pressing section III. to the left, and the rest of the tube is then washed out with and finally filled with the buffer to be used, and connected to the electrode tubes. To save time, all solutions are kept in the cold room before filling the apparatus. The apparatus is left in the bath to attain constant temperature, after which the electrode vessels are levelled by connecting them for a few minutes through a tube between the two upper stopcocks. The clockwork to the compensation is then started, and the boundaries are made by moving section III. back again, after which the current may be applied. If optical study of the boundaries is to be made right from the start, the compensation may be allowed to work for some time before the current is started, so that the boundaries are brought out into the region where they can be observed. However, this is not usually necessary, since the boundaries soon become visible in any event. If two components are observed, their rate of migration is estimated, and from this a rate of compensation chosen, so that a value corresponding to the arithmetic mean (the mobilities taken with their signs) will not move at all. Then one boundary will move downwards (relatively to the tube) at exactly the same speed as the other moves upwards, and at the end of the experiment, the two sections to the left will contain only one component, the two to the right only the other. In this way the separation capacity of the apparatus can be utilised to its full extent even though both components migrate very rapidly in the same direction. At the end of the experiment sections II. and III. are moved slightly to the left, the apparatus is taken out, the electrode tubes removed, and the contents of the sections can be pipetted out with capillary pipettes, without taking the sections apart. Each section holds 4 c.c. so that 8 c.c. of solution of each component can be obtained. In the larger apparatus, with 5 × 100 mm. cross-section, this volume will be increased to 100 c.c., but it will probably not take quite so high a voltage, on account of the wider tubes. If it is only desired to measure the mobilities it is not necessary to run the boundaries so far. The mobility can be determined by observation of the boundaries or by analysis of the contents of the sections in the usual way.

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[6] The glass apparatus was manufactured by the firm F. Hellige & Co., G.m.b.H., Freiburg in Breisgau, Germany.

[7] Cohen and Bruins, *Z. physikal. Chemie*, 1924, 113, 157.

(3) Observation of the moving boundaries of colourless substances cannot be followed so readily by ultra-violet photography as in the earlier apparatus, as this would necessitate the expense of using quartz both for the U-tube and for the large windows. The Töpler "*schlieren*" projection method has, however, been adopted with quite good results. In the usual arrangement [8] a Dallmeyer objective of *f* about 60 cm. with large aperture (10 cm.) is placed as near to the apparatus as possible. A lamp and a diaphragm are placed at about 100 cm. distance, on the same side of the thermostat. The image of the diaphragm is thrown on the other side of the apparatus, at about 100 cm. from the window. Here a projection lens is placed, partially covered by a vertically movable screen with a sharp edge. Instead of the projection lens a camera objective can be used; in this way the photographs (Fig. 4) were obtained.

This method has proved much superior to the earlier light absorption method, especially when studying mixtures. With one and the same cell thickness, moreover, any concentration can be used, instead of the very narrow limits of concentration which the earlier method permits. By suitable adjustment of the edge in front of the lens any gradient can be observed, and even very diffuse boundaries may be located accurately.

There are several ways in which the amounts of the different components present may be determined optically, if the boundaries are well separated, so that not only qualitative but quantitative electrophoretic analysis may be effected. In the light absorption method the photographs were microphotometred, and the concentrations computed from the photometric diagrams; the same procedure can be applied to the photographs obtained by the present method. The concentrations are obtained by graphic integration of the curves obtained.* The refractive index method originally suggested by the author and worked out by Lamm [9] for use in the ultracentrifuge and diffusion measurements may also be applied for the same purpose. For measurement of the migration of the boundaries, however, the above method is much more convenient.

(4) The potential source consists of a centre-tapped 2 × 1500 volt transformer, taking 100 m.a., with two half-wave mercury rectifying tubes of maximum peak inverse voltage of 7500 volts and maximum peak plate current 600 m.a. The filter circuit consists of a 20 Henry choke and a 4 μF condenser. The voltage fluctuations were small as the primary voltage was kept constant with an induction regulator. As in previous work current rather than voltage was measured, and a coulometer should be used for very accurate work especially if the voltage shows fluctuations.

Some Examples of the Application of the Apparatus.

(1) *Electrophoretic analysis of a mixture of R. phycocyan and R. phycoerythrin.*—These two proteins, which occur together in certain algæ, have been studied electrophoretically in detail by the author,[1] and by Pedersen: [10] the isoelectric points are 4·85 and 4·25 and the slope of the mobility p_H curve at the isoelectric points $du/dp_H = 10{\cdot}2 \times 10^{-5}$ and $14{\cdot}2 \times 10^{-5}$ cm.^{2} sec.$^{-1}$ volt^{-1} at 20° C. Thus the separation is most favourable in alkaline solutions where the difference in mobility is about 10×10^{-5}, both migrating in the same direction. Separation at such a considerable difference in mobility is a very easy matter, especially since the proteins can be dissolved in buffer solutions of low conductivity, allowing a very high voltage to be used. Since the separation of these proteins can otherwise be performed only by repeated crystallisation (frequently with considerable loss of the phycocyan which usually amounts to only 10 per cent. of the phycoerythrin), this method has considerable preparative value and has been so used in our laboratory with very good results. In one experiment the voltage was 880 volts (23·2 volts per cm. in the tube), the current 15·5 milliamp., the substances were dissolved in phosphate buffer $m/100$ p_H 6·96 of conductivity $0{\cdot}77 \times 10^{-3}$ at 0° C., the heat effect was therefore $(23{\cdot}2)^2 \times 0{\cdot}77 \times 10^{-3} = 0{\cdot}415$ watts per c.c. well below the maximum. The compensation was adjusted so that both boundaries migrated in opposite directions at the same rate. After two hours and twenty minutes the separation was completed: the cells on one side containing only phycocyan, those on the other only phycoerythrin. In separations with apparatus of the U-tube type one can of course never make use of the migration in the lowest U-shaped section which, being a dead volume, should be made relatively as small as possible: in our construction about 4·5 c.c.

(2) *Electrophoretic analysis of blood serum.*†—In this case the conductivity is rather high, so that the fact that the apparatus takes large currents is especially useful. The serum was dialysed against an phosphate buffer of p_H 8·06, the same buffer being used as supernatant fluid. A voltage of 7·25 volts per cm. was used. Fig. 4 shows a number of photographs of the

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* For a discussion of the quantitative application of the "*schlieren*" method in this manner see the work of Schardin.[8]

[8] See the usual handbooks of Practical Physics. A recent survey: H. Schardin, *Das Toeplersche Schlierenverfahren*, VDI-Verlag, Berlin, 1934.

[9] O. Lamm, *Z. physikal. Chemie, A*, 1928, 138, 313.

[10] K. O. Pedersen, *Unpublished measurements.*

† Full details about the application of the apparatus for this purpose will be given in a forthcoming publication.

upwardly migrating boundaries on the positive side (upper row) and the downwardly migrating boundaries on the negative side (lower row), taken at time intervals of twenty minutes. The fastest boundary is serum albumin, the other two represent serum globulin fractions of different mobilities. At least one more component becomes visible if the screen is raised a little (see the last photograph in the lower row). In this experiment a compensation movement of 7·7 mm. per hour was used in order to bring out the slowest boundary of the region where it is screened off by the glass plates (lower part of cell in upper row). By suitable compensation the experiment can be arranged so that the different components can be isolated.

Summary.

Some improvements in the experimental arrangement for electrophoresis are discussed, with special attention to the study of mixtures. It is shown that a very considerable increase in the applied potential gradient can be obtained by changing the shape of the U-tube, and, above all, by keeping the electrophoresis tube at a temperature in the neighbourhood of the density maximum for water (+ 4° C.), thus greatly reducing the risk of heat convection currents.

A modification of an earlier construction of electrophoresis apparatus is described, in which regard has been given to these points. The new apparatus has also provision for taking out samples of the separated fractions. The optical observation of the boundaries is made by an improved method depending upon refractive index (Töpler's *schlieren* method). For difficult separations large electrode vessels can be used, and a compensation arrangement, making it possible to obtain a large separation volume even if the components migrate in the same direction.

This work was performed in the Institute of Physical Chemistry of Upsala University. The author desires to express his thanks to Professor The Svedberg for the excellent facilities put at his disposal.

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THE ABSORPTION AND DIFFUSION OF WATER IN RUBBER.

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I. Introduction.

The course of absorption or desorption of liquids by colloidal materials under various conditions is a subject of great scientific and technical importance and there is already a mass of literature on the subject, for example, in connection with celluloid, leather, gelatine, and clays. The present paper deals only with the case of absorption of water by rubber; but it is anticipated that the results of this work may find some application or suggest lines of enquiry in other fields.

Most of the published work on the absorption of water by rubber is concerned with the amount absorbed under conditions of equilibrium with atmospheres of known humidity or with solutions of known vapour pressure, and comparatively little with time relations before equilibrium is established or during fluctuating conditions. That this non-equilibrium period is often important may be shown by the following typical cases of practical interest.

(*a*) One of the costly major operations in the preparation of raw rubber on the plantation is the drying of the rubber after coagulation and washing. This process is limited by the rate of diffusion of moisture through the rubber and any acceleration of the process would be of great economic importance to the industry.

(*b*) It is frequently necessary to investigate the amount of water which rubber will absorb under equilibrium conditions. As the time taken to reach equilibrium under ordinary test conditions may be many months it is important to decide to what extent the final absorption can be predicted from short period tests.

(*c*) In electric cables, especially submarine cables, where the dielectric is able to take up water from the sea, the various electrical properties which affect the transmission properties are differently affected by the spatial distribution of the absorbed moisture through the dielectric. Similar problems occur with solid insulators in which the surface resistivity and other electrical properties are differently affected by periodic changes of ambient humidity.

The study of these aspects of the subject requires the establishment of a satisfactory differential equation of diffusion of moisture through the rubber and it has previously been assumed that a simple equation which applies to the diffusion of gases applies equally well to the case of water. It is the purpose of this paper to show that the simple equation does not apply, to substitute a modified equation which agrees more nearly with observations, and to draw attention to important consequences of this departure from the simpler diffusion laws.

II. Theory of Time-Absorption Curve.

(1) Simple Gases in Rubber.

(*a*) **General Laws of Diffusion.**—In order to make clear the special behaviour of water it is recalled that simple gases obey Fick's and Henry's laws, the appropriate differential equation for the case where concentration varies in one dimension only being

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where c is the concentration at time t in a plane at a distance x from the origin measured in the direction of diffusion, and D is the diffusion constant. This is analogous to the case of conduction of heat.

(*b*) **Diffusion in an Infinite Sheet.**—The case of most frequent interest for experimental purposes is that of a sheet of thickness $2a$, and of such extent that edge effects may be neglected, initially free from the gas, but suddenly immersed at time $t = 0$ into gas maintained at a fixed partial pressure.

In diffusion experiments it is usual to measure the total quantity absorbed, and solutions for this case are given by Andrews and Johnston,[1] and McKay.[2] Their principal conclusions for our purpose may be expressed thus :—

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[1] *J. Amer. Chem. Soc.*, 1924, 46, 640.

(i) If Q and Q_m are the quantities of gas absorbed at times t and ∞ respectively, the degree of saturation as shown by Q/Q_m may be expressed as a series in terms of a single parameter $\tau = \frac{4a^2}{\pi^2 D}$ which may be called the Time Constant.

(ii) The curve connecting Q/Q_m with τ, which will be called the "Normal Gas Absorption Curve," is shown in Fig. 1 and can be closely represented over the whole range by a combination of two approximations as shown in the figure.

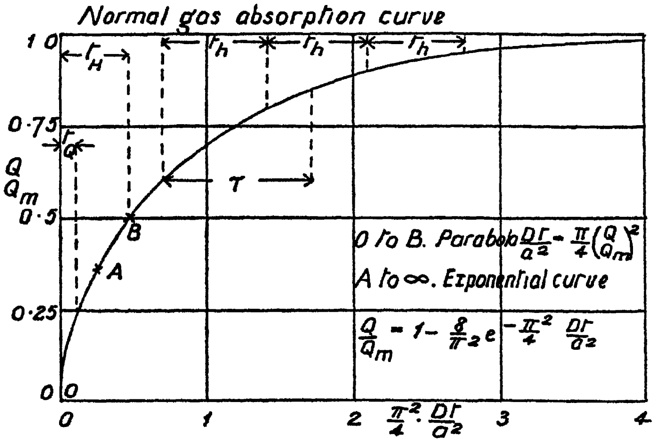

FIG. 1.

(2) Diffusion of Water Vapour in Rubber.

In previous literature on the subject[3] it has been assumed that diffusion of water through rubber can be expressed by the differential equation (1) applicable to gases; but in view of the complex nature of the absorption of water by rubber[4] it is desirable to examine this assumption more critically.

Since the absorption is largely due to the formation of a solution of water-soluble substances within the rubber it is to be expected that the rate of diffusion at any point will be proportional to the gradient of osmotic pressure instead of the gradient of concentration of water. In other words, the symbol c now represents quite different properties on the two sides of the equation (1). On the left it represents the concentration of water in the rubber, while on the right it is a function of the concentration of water-soluble substances in the absorbed water. Now the difference between the osmotic pressures of two aqueous solutions is proportional to the difference between the relative humidities (R.H.) of the atmospheres which would be in equilibrium with the solutions. Equation (1) must therefore be rewritten :—

$$\frac{\partial c}{\partial t} = D^1 \frac{\partial^2 h}{\partial x^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

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[2] *Proc. Physic. Soc.*, 1930, **42**, 547.

[3] *E.g.*, Andrews and Johnston,[1]; N. H. van Harpen, *Kautschuk*, 1931, **7**, 108.

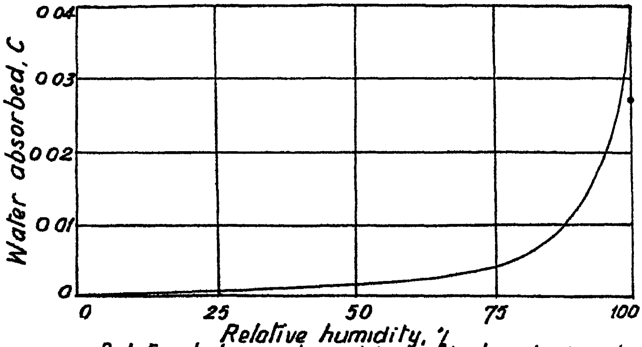
[4] Lowry and Kohman, *J. Physic. Chem.*, 1927, **31**, 23.

where h = relative humidity of the atmosphere which would be in equilibrium with the internal solution at x (to be called the "equivalent humidity"),

and D^1 = a constant depending on the rubber. (The possibility of its varying with the amount of water absorbed must be borne in mind).

Moreover, the relation between c and h can be determined experimentally by measuring the equilibrium absorption of water by rubber in solutions or in atmospheres of known relative humidity,[5] and is of the type shown in Fig. 2, the shape of the curve depending on the rubber. The vulcanised sample shown was made from commercial smoked sheet and contained 5 per cent. combined sulphur.[4]

It should be noted that c in Fig. 2 is the weight of water per unit weight of dry rubber, whereas in equation (2) it is the volume of water per unit volume of rubber plus absorbed water. As the amount of water is usually small this difference may be left out of account for the present in considering the shape of the relative humidity/absorption curve.



Relation between humidity and absorbed water in a typical vulcanised rubber.

FIG. 2.

Equation (2) may now be written

$$\frac{\partial h}{\partial t}\cdot\frac{\partial c}{\partial h} = D^1\frac{\partial^2 h}{\partial x^2}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This is the equation which is proposed to replace the commonly accepted equation (1). The consequences of the revised theory and the evidence of its validity are considered below.

III. Study of Time/Water-content Curve in Light of Revised Theory.

Since $\partial c/\partial h$ is not constant (see Fig. 2), the solutions of equation (1) cannot now be used either to determine c or h as a function of x and t or to obtain the total absorption at a time t by integrating c with respect to x. However, pending a solution to equation (3), some useful conclusions may be drawn which may be made the basis of experimental tests of the theory. It is proposed to consider several aspects of the problem, (*a*) to indicate in what way water diffusion is expected to differ from gas diffu-

[5] Lowry and Kohman,[4]; Daynes, *India Rubber Journal*, 1932, 84, 376.

sion, (*b*) to cite published work bearing on these predictions, and (*c*) where published information is lacking, to describe new experiments.

In this connection it is pointed out that the theory applies only to conditions in which equilibrium can be reached. Consequently it is necessary to leave out of consideration most of the published work on the drying of raw rubber, where the initial and final states are usually indefinite, on the drying of freshly coagulated rubber, which appears to be a very complicated system, and on the absorption of water by unvulcanised rubber at very high humidities, where equilibrium is seldom reached.

(1) Time-absorption Curve within Narrow Range of Humidity.

(a) If a sheet saturated at relative humidity h_1 is transferred to another humidity h_2 so close to h_1 that $\partial c/\partial h$ may be considered constant from h_1 to h_2, the time-absorption relation is similar in form to the solution of equation (1) writing $D^1\Big/\frac{\partial c}{\partial h}$ for D and $\frac{Q - Q_t}{Q_m - Q_t}$ for Q/Q_m, where Q_t = quantity of water uniformly absorbed initially. The expression $\frac{4a^2\frac{\partial c}{\partial h}}{\pi^2 D^1}$ now takes the place of $\frac{4a^2}{\pi^2 D}$ as the time constant of the curve. Since $\partial c/\partial h$ increases with humidity and also, usually, with the hygroscopicity of the rubber, the time taken to reach a given value of $\frac{Q - Q_t}{Q_m - Q_t}$ will increase with these factors also, whereas if the simple gas diffusion equation (1) applied the time constant would be independent of them.

(b) Confirmation of this prediction has been found with finely rasped samples of unvulcanised and vulcanised rubber[6] and with gutta percha and Paragutta, a submarine cable insulating material consisting of deresinated balata, deproteinised rubber, and wax.[7]

(c) In most of the experimental work to be described in this paper, rubbers of known composition which had been made up in the laboratory for other purposes were used. They were selected to cover a wide range of behaviour in regard to water absorption rather than to isolate the effects of the constituents of natural rubber or to exhibit the influence of particular

TABLE I.

	Rubber Sample.					
	A.	B.	C.	D.	E	F.
Smoked sheet rubber	100	100	100	100	100	—
Para rubber	—	—	—	—	—	100
Zinc oxide	62	62	50	65·5	—	—
Gas black	30	30	1·5	—	—	—
Sulphur	6	7·2	3	2·5	5·3	5·3
Triphenylguanidine	2	2·4	—	—	—	—
Mercaptobenzthiazole	—	—	0·7	—	—	—
Tetraethylthiuram-disulphide	—	—	—	0·5	—	—
Alkali tire reclaim	—	40	—	—	—	—
Paraffin wax	—	—	3·5	—	—	—
French chalk	—	—	40	—	—	—

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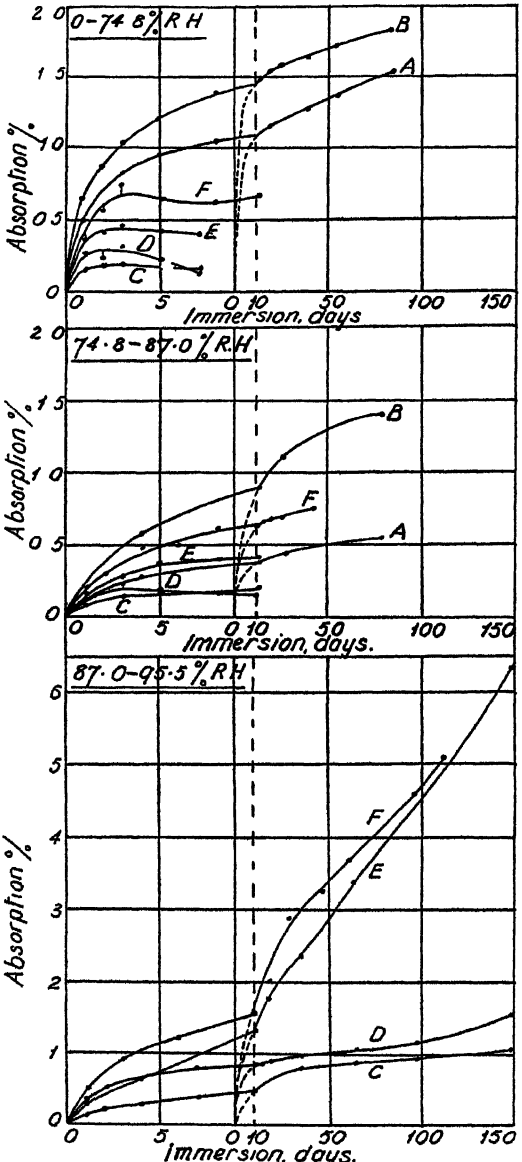
[6] Daynes [5], *loc. cit.*

[7] Kemp, *Bell Laboratories Record*, 1931, May, p. 422; *India Rubber World*, 1931, June, p. 56.

ingredients or conditions of vulcanisation. The ingredients are shown in Table I. All the samples were vulcanised normally (*i.e.*, nearly to maximum tensile strength) except those from mixings having a high percentage of sulphur, in which cases samples which did not exhibit "blooming" of sulphur to the surface were chosen to avoid complications due to loss of free sulphur in handling. Since this involved over-vulcanisation the ageing properties of the rubber in those cases were inferior.



Absorption curves for rubber strips in saturated salt solutions

FIGS. 3, 4, 5.

To minimise the thickness in one dimension, most of the specimens used were parts of the outer rings from which Schopper tensile test rings had been punched, the dimensions being: internal diameter, 52·3 mm.; axial thickness, about 5 mm.; radial thickness 2·3 mm. One specimen D, however, was a disc 0·73 mm. thick and 44 mm. in diameter.

After preliminary drying *in vacuo* for 4 days at 70° C., the specimens were immersed in an appropriate salt solution in stoppered bottles and maintained at 34° C. At intervals the specimens were withdrawn, superficially dried, weighed in tared, stoppered bottles and re-immersed. The solutions were kept saturated by the presence of an excess of the salt. The salts used, and their equivalent humidities at 34° C. were as follows [8]: sodium chloride, 74·8 per cent. R.H.; sodium sulphate, 87·0 per cent. R.H.; potassium sulphate, 96·5 per cent. R.H. After the preliminary drying each specimen was placed in the sodium chloride solution and weighed

[8] Leopold and Johnston, *J. Amer. Chem. Soc.*, 1927, 49, 1924.

at intervals until equilibrium was reached, then transferred to the next solution in order of humidity, and so on. In some cases the whole series was not completed, since equilibrium was not reached in a reasonable time.

The absorption, in excess of the final absorption at the previous humidity, expressed as a percentage of the dry weight is shown in Figs. 3, 4 and 5.* In some cases the absorption was so small that the half-saturation period t_H could not be determined accurately. The immersion of A and B had to be longer than that of the other specimens, and, as it was thought that the failure to reach equilibrium might be due to oxidation, the specimens were transferred to the second solution without waiting for equilibrium; they were not immersed in the third solution. Specimen D behaved in a peculiar way, the absorption in the solutions of lower humidity rising to a maximum and then decreasing, as if soluble material were being extracted; this is not uncommon with certain rubbers. Specimens E and F, which were expected to have bad ageing properties, did not reach equilibrium at the highest humidity.

In spite of the errors inherent in these small measurements it is evident that, with any of the rubbers tested, the half-saturation-period increases rapidly with the mean humidity over which the absorption takes place, as predicted by the osmotic theory. Further, there is a rough, but quite distinct parallelism between the hygroscopicity of the rubber and the half-saturation period. (In this comparison sample D must be excluded since it differed in dimensions from the others.)

(2) Time-absorption Curve over Wide Range of Humidity.

(a) Although the time-absorption curve for a rubber changing from equilibrium at one humidity to equilibrium at a much higher humidity cannot be calculated without the complete solution of equation (3), the following considerations will throw some light on the general shape of the curve. The concentration of water, and therefore the value of $\partial c/\partial h$, at each point in the rubber increases continuously with time. For each increment in "equivalent humidity" both the capacity of the rubber to absorb water and the "time constant" of the time/equivalent humidity curve increase rapidly. These effects may be represented in a general way as a modification of the "normal gas absorption curve" by continuously expanding absorption and time scales. These effects would be more marked the higher the hygroscopicity of the rubber and the higher the humidity of exposure.

The effect of variation in $\partial c/\partial h$ may be represented by a similar variation of specific heat in the analogous case of thermal conduction. If a sheet of metal, for example, at a uniform temperature of 0° C. were immersed in boiling water and the specific heat of the metal increased rapidly between 75° C. and 100° C., the heat absorption would follow the same course as water absorption by a rubber sheet. In the later stages, not only would the quantity of heat involved in changing the average temperature by a given amount be greater, but also the approach of each volume element to its final temperature would become slower.

(b) Andrews and Johnston [1] have shown that when sheets of a given rubber of various thicknesses are immersed in water and the amount of water absorbed, expressed as a fraction of the saturation value, is plotted against time/(thickness),^{2} all the points lie on a single curve; but this curve differs in shape from that predicted from equation (1), the initial rate of rise being relatively too great. The difference in shape was attributed by the authors to variation in structure through the sheets due to calendering, but it now appears that equation (3) is sufficient to explain both the variation of rate of absorption with thickness (section (3)), and the then unexpected shape of the time/absorption curve.

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* In this, and also Figs. 6, 8, 9 and 10, two time scales are used, the earlier part of each curve being plotted on an open scale and the later part on a closer scale, with the earlier part shown dotted to indicate the shape of the complete curve.

Confirmation of the above theory for cases in which equilibrium has been reached at lower humidities is found in the work of Fry [9] and of Messenger and Scott,[10] both using crêpe rubber, and of Kemp [7] using gutta percha and Paragutta.

A few confirmatory observations are available to show the variation of time/absorption curve with hygroscopicity of the rubber. These are in the work of Lowry and Kohman [4] who examined portions of a sample of commercial smoked sheet washed for various periods and of Boggs and Blake [11] working with chemically purified rubber hydrocarbon.

(c) The shape of the time-absorption curve over a wide range of humidity is shown by the following experiments.

In order to obtain equilibrium in a short time and so reduce the risk of oxidation effects, very thin sheets both of substantially unloaded vulcanised rubber, were used and a final humidity of 96·5 per cent. R.H. was adopted instead of 100 per cent. The available materials were (*a*) golf ball tape about 0·16 mm. thick and (*b*) sheet made from vulcanised latex about 0·13 mm. thick, which would contain more of the water-soluble constituents of the natural rubber than (*a*).

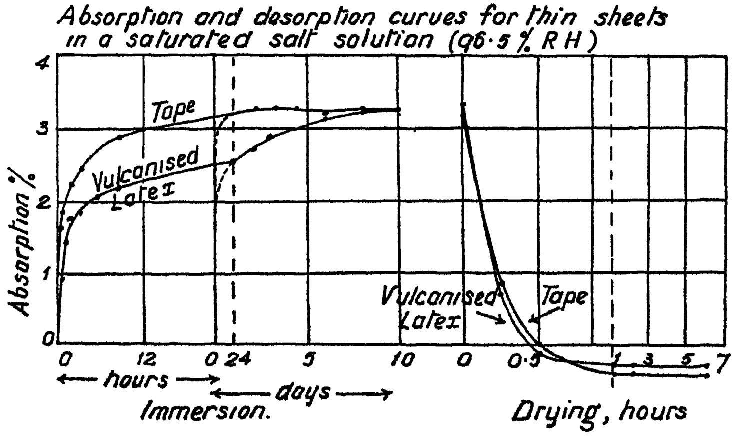

FIG. 6.

After preliminary drying, the specimens were immersed in saturated solutions of potassium sulphate at 34° C. and were taken out at intervals, superficially dried, and weighed in tared, stoppered bottles. Similar samples, which had been soaked in the solution for 11 days at 34° C., were dried in a desiccator at 34° C. and weighed at intervals until constant in weight.

The absorption and desorption curves are shown in Fig. 6. It will be seen that in both cases, on drying, the weight falls to a little below its original value before immersion. If, as seems probable, this is due to extraction of water-soluble substances, it may be assumed that the later part of the absorption curve has been somewhat flattened thereby.

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[9] *India Rubber Journal*, 1927, 73, 513.

[10] *Res. Assn. Brit. Rubber Manufacturers, Laboratory Circular*, No. 46, 1929.

[11] *Ind. Eng. Chem.*, 1926, 18, 224.

The analysis of the absorption curves is shown in Table II.

The following results, which are in accordance with the osmotic theory, will be noted from the table :—

(i) The shape of the time-absorption curve differs from that of the normal gas-absorption curve in the manner predicted.

The half-value-period t_h in lines 2 and 3 is much greater than the value $1{\cdot}43 t_H$ appropriate to a simple gas and increases with time.

TABLE II.

Portion of Curve.	Time Occupied, Hours.	
	Tape.	Vulcanised Latex Sheet.
0 to $\frac{1}{2}$-saturation (t_H)	0·5	2·0
$\frac{1}{2}$ to $\frac{3}{4}$-saturation (t_h)	2·7	15
$\frac{3}{4}$ to $\frac{7}{8}$-saturation (t_h)	3·8	55

(ii) The departure from the form of the normal gas-absorption curve is more marked with one rubber (vulcanised latex) than the other ; the curves cannot be superposed merely by an adjustment of the time scale of one curve. This would be expected if the shapes of the humidity/absorption curves differed.

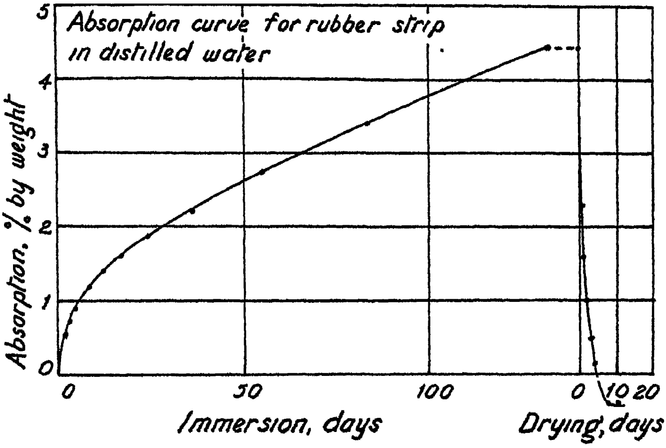

FIG. 7.

Similar effects were shown in absorption and desorption curves with a specimen of rubber C as described in Section III. (1). The technique was similar except that the liquid was distilled water which was renewed frequently to avoid contamination. The results are shown in Fig. 7.

(3) Variation of Saturation or Drying-period with Thickness.

(a) The theory of Andrews and Johnston [1] that the time taken to reach a given stage of saturation varies as the square of the thickness of the sheet can easily be shown to be consistent with the new equation (3) as well as the old equation (1).

(b) The experimental results of Andrews and Johnston are therefore consistent with the new theory as also are those of Boggs and Blake [11] who found that, with sheets of different thickness of one rubber, the early portions of the time-absorption curves coincided when absorption was expressed in terms of gain in weight per unit surface area. This result follows from either theory if the time-absorption curves are parabolic, as is the case with the curves in question within the accuracy of measurement of the printed curves.

Van Harpen [8] has shown that the "time of drying" of raw rubber varies as the square of the thickness of the sheet.

(4) Drying Curve.

(a) According to equation (1) the time curve for a gas diffusing into a sheet is simply the inverse of that for a gas diffusing out. This is not the case for water vapour behaving in accordance with equation (3), and some important conclusions may be drawn as follows:—

Shape of Curve.—One would expect the shape of the desorption (or drying) curve to differ from that of the absorption (or soaking) curve in that the approach to the asymptote would not be so slow in the former case, especially in the later stages of the process. The time "constant" $\frac{4a^2\frac{\partial c}{\partial h}}{\pi D^1}$ should now decrease with time instead of increasing, causing the final approach to the end-point of the drying process to be much quicker.

Time Required for Drying.—The time required for the loss of a given amount of water from saturated rubber should be very much less than that required for the absorption of the same amount by dry rubber. Refer again to Fig. 2 and consider the differences of equivalent humidity between some point well inside the rubber and another just within the boundary which may be assumed either dry or saturated as the case may be. In absorption it is seen that, by the time half-saturation (2 per cent. absorption) is reached at the point inside the rubber, the equivalent-humidity difference between the two points has fallen to 4·5 per cent. of its original value, whereas after desorption to the same state it is still 95·5 per cent. of its original value. After absorption to 9/10 saturation and drying to 1/10 saturation the equivalent humidity differences are about 0·5 per cent. and 72·5 per cent. respectively. The bulk of the water, therefore, is absorbed under the influence of a low osmotic pressure difference in soaking and is lost under the influence of a high osmotic pressure difference in drying.

Similarity of Absorption and Desorption Curves over a Narrow Range of Humidity.—Effects (i) and (ii) noted above arise from the great curvature of the humidity-absorption relationship of rubber. If the humidity changes were confined within narrow limits so that $\partial c/\partial h$ remained constant over the whole range, the differences between the shapes and time-scales of the absorption and desorption curves should disappear.

(b) Time Required for Drying.—The great differences between the times required for absorption and desorption is shown by the results of Fry [9] with raw rubber, and of Cooper and Scott [12] with cold-cured rubbers.

This more rapid drying or desorption over a given range of humidity must not be confused with the slower desorption observed by Kemp

[12] *Res. Assn. Brit. Rubber Manufacturers, Laboratory Circular*, No. 65, 1930.

(Section III (1)) in which the absorption and desorption took place over mutually exclusive ranges of humidity.

H. Bradley, A. T. McKay, and B. Worswick,[13] in a very similar investigation on diffusion of water vapour in leather, found that between 0 and 30 per cent. R.H. the time for drying was much greater than for "wetting," the reverse of the effect observed with rubber; but the curvature of the humidity-absorption graph also was opposite in direction to that of rubber over the range concerned.

(c) Comparison of Absorption and Desorption Curves.—The relative shapes and time scales of the absorption and desorption curves are shown in the experiments described in Section III (2) (Figs. 6 and 7). There the drying was so rapid that it is not possible to analyse the curves accurately, but it will be seen that in drying there was no very slow approach to the final value as in absorption, and that both samples were dry within a very short time compared with that required or saturation.

The main object of the next experiment was to study the relative rates of attainment of equilibrium in absorption and desorption over various restricted ranges of humidity under conditions of rapid attainment of equilibrium, and therefore, less risk of interference by oxidation. In particular, it was intended to obtain confirmation of the prediction from the osmotic theory that over a humidity range so small that the humidity-absorption relationship could be considered linear, the half-saturation and half-drying periods would be equal. Unfortunately, accurate determinations under such conditions are extremely difficult, and the experiments were therefore confined to demonstrating a simpler case of the same problem, *viz.* that if a given humidity range is divided into two smaller ranges, so that the humidity-absorption relationship is more nearly linear in each small range than over the whole range, then in each small range the half-saturation and half-drying periods will be more nearly equal than those for the whole range. It was intended, also, to compare the shapes of the absorption and desorption curves, although the actual shape in either case could not be predicted, owing to the irregularity of size and form of the finely divided rubber.

The rubbers used for these tests were B and E, as described in Section III (1). They were finely divided by rasping, spread on watch-glasses as is usual in the R.A.B.R.M. method of determination of water absorption (Daynes),[5] and exposed at 20° C. to atmospheres of one humidity, weighings being taken at short intervals up to equilibrium. The watch-glasses were

TABLE III.

Rubber.	Humidity Range. Per Cent. R.H.	t_H in Min. for—		Ratio $\frac{\text{H.S.P.}}{\text{H.D.P.}}$.
		Rising Humidity (H.S.P.).	Falling Humidity (H.D.P.).	
B	0–86·8	84	24	3·5
	0–75·0	18	15	1·2
	75·0–86·8	160	73	2·2
E	0–86·8	27	9	3·0
	0–75·0	< 10	6	$< 1·7$
	75·0–86·8	42	18	2·3

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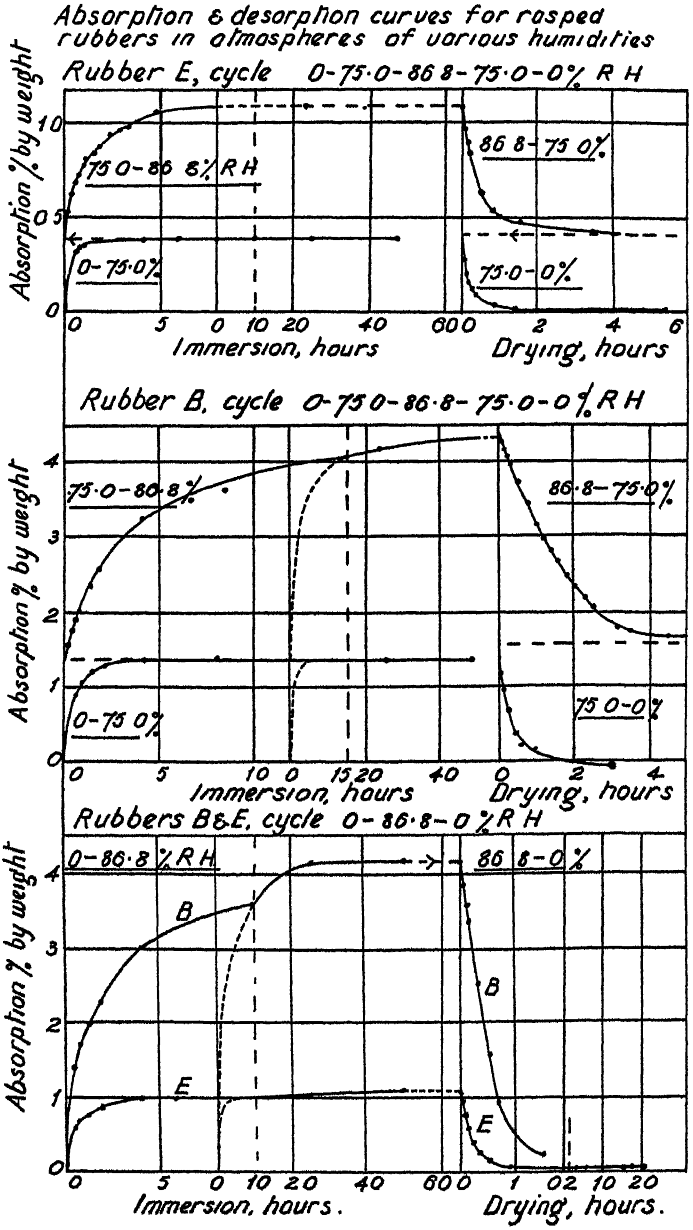
[13] *Report No.* 21. *The British Boot, Shoe & Allied Trades Research Association*, July, 1928; *J. Inst. Soc. Leather Trades' Chemists*, 1929, 13, 10, 87.

then transferred to jars containing atmospheres at other humidities as required and the process repeated. Each of the two rubbers was subjected in this way to the following cycles of exposure :—

(*a*) 0 per cent. R.H. — 86·8 per cent. R.H. (sodium sulphate) — 0 per cent. R.H.



FIGS. 8, 9, 10.

(*b*) 0 per cent. R.H. — 75·0 per cent. R.H. (sodium chloride) — 86·8 per cent. R.H. — 75·0 per cent. R.H. — 0 per cent. R.H.

The absorption and desorption curves are shown in Figs. 8, 9 and 10.

The values of t_H under various conditions are shown in Table III., together with the ratio of t_H for rising and for falling humidities.

It is seen that the osmotic theory is confirmed in that: (*a*) the ratio half-saturation-period (H.S.P.)/half-drying-period (H.D.P.) for the smaller ranges of humidity 0-75·0 per cent. and 75·0-86·8 per cent. is greater than unity, but is nearer unity than for the whole range 0-86·8 per cent., and very much less than that observed in previous experiments (Figs. 6 and 7) with still larger ranges of 0-100 per cent. and 0-96·5 per cent.; (*b*) the higher the hygroscopicity of the rubber, and the higher the mean humidity of the atmosphere during the change, the greater is the value of t_H.

In Figs. 8, 9 and 10 the difference in shape between absorption and desorption curves is very noticeable where there is a wide change of humidity. The drying curve is comparatively straight at first and sharply curved at the end. The reverse is found in the absorption curve. This difference is not so clear in the more restricted changes of humidity, particularly over the range 0-75 per cent. R.H., where $\partial c/\partial h$ is known to be nearly constant.

IV. Conclusions.

We may now summarise the main results of the investigation.

(1) Predictions based on the differential equation (3) are substantially confirmed by the results of various workers, and the simpler gas diffusion equation (1), which is usually assumed, is shown to be inapplicable to the case of water vapour in rubber. The confirmation being somewhat indirect, it would be desirable to obtain more direct evidence by measuring the rate of diffusion of water vapour through thin rubber films under equilibrium conditions with various small differences of humidity between the two sides of the film. In that way it would be possible to obtain more precise information as to the relation between rate of diffusion and osmotic pressure gradient, and thus as to the extent to which the "diffusion constant" D' is independent of the water vapour concentration.

(2) When a sample of rubber changes from equilibrium at one humidity to equilibrium at a much higher humidity, the time-absorption curve is characterised by a rapid initial rise and an approach to equilibrium that is much more prolonged than if the simple gas-diffusion equation applied. The higher the humidity being approached, and generally, the greater the hygroscopicity of the rubber, the more marked is this slowness of approach to equilibrium, and the greater is the time required for, say, half the total change in water-content to occur.

(3) When a sample of rubber changes from equilibrium at one humidity to equilibrium at a neighbouring humidity, the time required for, say, half the change in water content increases with the mean humidity and, generally, with the hygroscopicity of the rubber.

(4) When desorption takes place in a sample of rubber changing from equilibrium at one humidity to equilibrium at a considerably lower humidity:

(*a*) the early part of the time/water content curve is comparatively straight and the approach to equilibrium fairly abrupt;

(*b*) the time required for, say, half the change in water content to occur is much less than the corresponding time in the process of absorption between the same humidity limits;

(*c*) the smaller the range of humidity over which the change occurs the more nearly is the curve similar in shape and time scale to that which would occur with a rising humidity over the same range.

(5) When rubber sheets which are identical except in thickness are subjected to changes in ambient humidity, the time required for, say, half the change in water content to occur varies as the square of the thickness. In this respect there is no difference between the predictions of the old and new diffusion equations.

More generally we may say that the time relations in absorption and desorption of water vapour in rubber are determined very largely by the shape of the humidity-absorption curve for the particular rubber under consideration and that the further study of such relations in connection with practical problems demands a solution of the new differential equation.

V. Summary.

A new differential equation of diffusion is put forward to represent the movements of water vapour through rubber in accordance with the osmotic theory of absorption.

Experiments are described which, together with the evidence quoted from existing knowledge, confirm a number of predictions as to differences between the absorption of a gas and of water vapour by rubber. These predictions deal with the shapes of the absorption- and desorption-time curves between narrow and wide limits of humidity, the relative times required for absorption and desorption, and the variation of absorption and desorption periods with thickness of the rubber sheet. The results are definitely inconsistent with the simple gas-diffusion theory which is often assumed to apply to water in rubber. It is established that the shape of the humidity-absorption curve is a dominant factor in determining time-water content relations. Except for changes over very restricted ranges of humidity, the absorption- and desorption-time curves are of different shape, and desorption is much more rapid than absorption. The periods required for absorption and desorption are greater, the higher the humidity and the higher the hygroscopicity of the rubber. The law that the time required to reach a given stage of saturation varies as the square of the linear dimensions of the sample (the shape being constant) is equally true for diffusion according to the old and new equations.

Future progress in the application of the osmotic theory to a number of practical problems, some of which are indicated, will depend largely on the solution of a differential equation of the type:

$$\frac{\partial h}{\partial t} = D^1 f(h) \frac{\partial^2 h}{\partial x^2}$$

in which the form of the function $f(h)$ varies with the water-absorbing constituents of the rubber.

Acknowledgment is made of the kindness of the Board of Management of the Rubber Research Association in permitting the publication of this investigation, which was communicated to their members as *Laboratory Circulars*, Nos. 98 and 108, June, 1932, and February, 1933.

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THE SURFACE TENSION OF INTENSIVELY DRIED α-SULPHUR TRIOXIDE.

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Smits and Schoenmaker [1,2,3,4] investigated the vapour pressure of intensively dried sulphur trioxide. Sulphur trioxide was chosen because it is itself a powerful dehydrating agent. It was supposed that the self-drying effect would assist the added drying agent, so that the effect of intensive drying would be more rapidly attained than with, for example, benzene. Attention does not seem to have been drawn to the obvious fact that the moisture in benzene is presumably mechanically mixed with it, while moisture in sulphur trioxide must be almost entirely present as sulphuric acid, since even with a very low concentration of water, the equilibrium

$$SO_3 + H_2O \rightleftharpoons H_2SO_4$$

is well over to the right hand side. If the effects of intensive drying are real, one would expect these effects to show up in any sample of sulphur trioxide which had not been too lavishly exposed to moisture.

Smits worked with the pure α, β, and γ forms respectively. He was able to show that the α and γ modifications were heterogeneous, the pseudo-components being in internal equilibrium. When this equilibrium was disturbed it re-adjusted itself at a rate which was slower, the more intensive the drying had been. He was thus able to separate the " pure " allotropes into fractions having very different vapour pressures. Indeed, he found that mere distillation of the sulphur trioxide, without passing the vapour over phosphorus pentoxide, was sufficient to convert it to the intensively dried state. Smits' work leaves no doubt as to the complexity of at least the α and γ modifications of sulphur trioxide. Only the γ form is stable.

The present work was undertaken with a view, firstly, to providing further evidence of the complexity of α-sulphur trioxide, and, secondly, of throwing some light on the molecular constitution of intensively dried sulphur trioxide by means of the Sugden parachor. This latter formula requires a knowledge of the density, and this was also determined during the measurements. The question of the structural formula of sulphur trioxide is a very debatable one, but Sugden [5] himself, on the basis of existing measurements of the density and surface tension of (not intensively dried) sulphur trioxide, assigns the formula

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* We are indebted to Mr. H. L. Fanshaw, M.Sc., for some preliminary work along these lines.

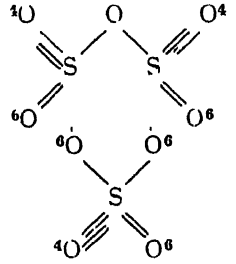
[1] Smits and Schoenmaker, *J. Chem. Soc.*, 1924, 2554.

[2] *Ibid.*, 1926, 1108.

[3] *Ibid.*, 1926, 1603.

[5] Sugden, *The Parachor and Valency* (Routledge), 1930.

[4] Smits, *Z. physikal. Chem.*, 1931, 152, 432.



in which the numerals indicate unshared electrons. In other words, he assumes the existence of the S_3O_9 molecule at the temperature for which he took his values of surface tension and density.

Assuming the existence of Smits' pseudo-components, as indeed seems necessary with sulphur trioxide, the question arises of whether they are isomers, or polymers of one another, using these terms in their widest sense. When the *T*—*X* diagram for a pseudo-binary system exhibits a eutectic, we seem justified in concluding that the components are not polymers. The converse, however, is not true. When there is no eutectic, as in the SO_3-pseudo-system, it does not follow that the components are polymers. We remain, therefore, in ignorance as to the nature of the pseudo-components of sulphur trioxide.

It was thought that further information regarded the nature of the pseudo-components could be obtained by using the following principle: intensive drying of the sulphur trioxide by passing its vapour repeatedly through phosphorus pentoxide would freeze the equilibrium, thus causing the substance to exhibit binary behaviour. The sulphur trioxide would then be distilled in fractions and some physical property of each successive fraction measured. The magnitude of this property would either remain constant or show a change with fractionation, but the interpretation of the result would depend upon the particular property concerned. We selected surface tension as a suitable physical property since it could be interpreted in the light of the parachor to give information regarding constitution. On the other hand, surface tension appears to be related to molecular association, so that a change in surface tension, as such, would point to the polymeric nature of the pseudo-components.

Schenck[6] made the first reliable measurement of the surface tension of sulphur trioxide, which had been dried by phosphorus pentoxide to a considerable extent. Twenty years later, Berthoud[7] repeated the determination under similar conditions, but neither author attempted to fractionate.

The capillary rise method of determining surface tension is the only feasible one with sulphur trioxide, and this was the method used by previous workers, although the technique is notoriously difficult. Considerable attention has been given in recent years to refining this method,[8,9] but such refinements could hardly be applied in our case.

[6] Schenck, *Liebig's Ann.*, 1901, **316**, 1.
[7] Berthoud, *J. Chim. Physique*, 1923, **20**, 77.
[8] Harkins, *J.A.C.S.*, 1919, **41**, 499.
[9] Mills and Robinson, *J.C.S.*, 1927, 1823.

Adherence or otherwise to the Ramsay-Shields relation used to be considered evidence as to whether or not a liquid is associated, but this view is not now generally held. Nevertheless, as we worked at two temperatures, we were able to evaluate the temperature coefficient of molecular surface energy for what it is worth. Unquestionably, a value of this coefficient of less than 2·12 does in many cases indicate association.

Experimental.

The apparatus is shown in the diagram (Fig. 1). Hard glass was used throughout. A and B are receptacles for the liquid sulphur trioxide, C and D, U-tubes to contain the drying agent-phosphorus pentoxide. In order to remove from the glass tiny capillaries which might occlude moisture, we adopted a method similar to that employed by Smits and his co-workers,[10] who heated their glass apparatus just to the softening point. The whole apparatus was wound with asbestos paper and nichrome resistance wire. During the heating a current of air, dried by passage through a large calcium chloride tube, two sulphuric acid bubblers, and two phosphorus pentoxide towers, was passed through the apparatus. The temperature was such that the apparatus was slightly distorted by the heating, so that there is no question of capillaries not being fused up.

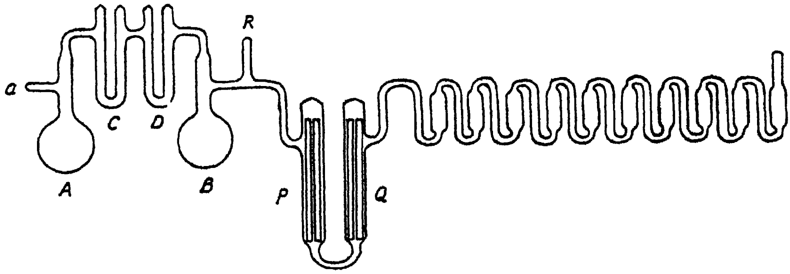


Fig. 1.

Phosphorus pentoxide from a freshly opened bottle was introduced into the U-tubes. Approximately 5 grams of phosphorus pentoxide were placed in each U-tube. During the filling process, dried air was passing through the apparatus continually. The U-tubes were sealed off immediately after filling, and the sulphur trioxide introduced through the end *a*.

The sulphur trioxide used was a 100-gram sample from Kahlbaum. It had been subject to self-drying for twenty-five years, since it was a museum sample of that age. Between 40 and 50 grams of sulphur trioxide were introduced. It was distilled into the evacuated apparatus in the usual way, and the apparatus sealed off at *a*.

The sulphur trioxide was distilled from A to B and from B to A alternately. A distillation took from one to two hours, the temperature of the hot flask being raised finally to 70°-80°.

The limbs P and Q (Fig. 1) of the U-tube contained two hard glass capillaries, resting loosely in them. To the right were ten bulbs for density measurements. Scratches were made on the capillaries at intervals of about 1 cm. for points of reference. The capillaries, after careful cleaning, were heated to redness before insertion in the U-tube.

Capillary rises were measured by means of a cathetometer, reading to 0·001 cm. The scale of the instrument was calibrated against a standard scale.

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[10] Smits, de Liefde, Swart and Claasen, *J.C S.*, 1926, 2658.

The sulphur trioxide was distilled through the phosphorus pentoxide forty-three times over a period of four months, before measurements were taken.

Surface Tension Measurements.

After completion of the drying period, the liquid sulphur trioxide was condensed in the surface tension apparatus, surrounded by a water-bath, which was kept at 20° by immersing in it a glass spiral through which water from a thermostat was circulated. When the measurements at 50° were commenced, an error in the design of the apparatus became apparent; the limbs of the U-tube should have been connected by a transverse tube to equalise the pressure. At 20°, the vapour pressure difference due to a small difference of temperature on either side was so slight that no difficulty was experienced in keeping the liquid at a constant level in the U-tube, as evidenced by check readings with the cathetometer. At 50°, however, the vapour pressure is much higher (*cf.* Smits) and the liquid level oscillated rather rapidly. It was only possible to get results at this temperature by having one observer control all the temperatures, while the other took readings. This could only be accomplished by setting the cross-hair of the telescope on the slowly moving outer meniscus and simultaneously reading the capillary height on a thermometer scale placed in the bath. Fortunately both levels were in the field of vision. The accuracy of the 50° measurements is low and useless for deciding on the homogeneity, or otherwise, of the fractions. The mean of several score determinations, however, is felt to be a quite good average value for 50°. Under the circumstances, no better temperature control was attempted than that of a 4-litre beaker of water heated by a small flame. In any case, the surface tension is small and not very sensitive to temperature. The position in the capillary of the upper meniscus was noted in reference to the scratches in the tube, in case the bore should be irregular.

The capillary rise of the most volatile fraction having been measured at the two temperatures, the same fraction was distilled to the density bulb at the extreme end of the apparatus and the bulb sealed off. In this way nine different fractions were measured and sealed off. The surface tension of the tenth fraction remaining in the apparatus was also measured. All nine fractions were measured and sealed off within ten days (one day separated the manipulation of the fifth and sixth fractions).

After completion of these measurements, the radii of the capillaries were determined by the mercury thread method, using mercury purified in the usual way. The capillaries were then cut into short lengths and the bores examined in a high power microscope. The deviation from a a true circle was in every case slight. The mean radius of the first capillary was 0·03595 cm., the deviation at any point being always in the fifth decimal. The other capillary had a mean radius of 0·03571 cm., but different sections varied in the fourth decimal.

From ten to twenty readings of capillary rise were made on each fraction. The appropriate value of the radius was used, corresponding to the position of the upper meniscus in the capillary. The densities used in calculation were the mean values for 20° and 50°. The angle of contact was assumed to be zero, as our predecessors assumed.

The diameter of the limbs of the U-tube carrying the capillaries was somewhat greater than 1 cm. There is always the difficulty of deciding what to take as the bottom level when measuring the capillary rise. We always took the lowest level of the outer meniscus, so our results should be, if anything, high.

Densities.

Within one hour of the sealing off, the sulphur tri-oxide in each bulb was run into the narrow limb and the bulb placed in a water bath at 20°.

The inside diameter of the narrow limbs was about 4 mm. The vertical distance between the meniscus and a reference scratch on the glass of the bulb was measured by a cathetometer with an accuracy of 0·01 cm. The temperature of the bath was now raised to 50° and the level of the meniscus again noted. The bulb was then weighed. Finally the bulbs were all opened, the sulphur tri-oxide destroyed, the bulbs filled with distilled water to the same levels and in each case weighed. The empty bulbs were then weighed.

Melting Points.

Determinations of the melting ranges of each fraction were made from one to two weeks after they had been sealed off. Prior to melting, the liquids had to be solidified by chilling in ice and salt.

The temperature was then raised slowly in a well-stirred water bath and the temperature held constant for some time as soon as signs of incipient fusion could be detected. Since fusion in no case took place at a constant temperature, the extreme limits of the range are somewhat indefinite.

Numerical Results.

DENSITY AND SURFACE TENSION.

Fraction No.	$d^{20°}_{4°}$.	$d^{50°}_{4°}$.	Surface Tension in dynes/cm.	
			20°.	50°.
1	1·919	1·781	31·11	26·02
2	1·934	1·780	31·41	26·16
3	1·889	1·782	29·73	25·65
4	1·933	1·728	30·46	25·74
5	1·897	1·781	31·19	—
6 *	1·889	1·793	31·42	24·99
7	1·948	1·783	31·84	25·50
8	1·937	1·781	31·34	25·48
9	1·932	1·783	31·82	25·41
10	—	—	31·53	—
Mean Values of Density	1·920	1·783	—	—

* Large experimental error in this determination of density, due to the liquid being confined in the wider limb.

The following are the results of previous workers :—

Density.

Schenk [6] $d^{20°}_{4°}$ 1·909 (interpolated) $d^{50°}_{4°} = 1·773$

Lichty [11] $d^{20°}_{4°} = 1·9229$ $d^{50°}_{4°} = 1·782$ (interpolated)

Berthoud [7] $d^{20°}_{4°} = 1·920$ $d^{50°}_{4°} = 1·783$

Surface Tension.

Schenk [6] γ at 20° $= 32·70$ γ at 50° $= 27·61$

Berthoud [7] γ at 20° $= 33·99$ γ at 50° $= 28·55$

Melting Points.

Different samples commenced to melt at temperatures varying from 11° to 26·9°, and melting took place over ranges varying from 4° to 35°.

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[11] Lichty, *J.A.C.S.*, 1912, **34**, 1440.

Discussion of Results.

The densities for 20° were first calculated. It was thought that the relatively large variation, between 1·889 and 1·948, represented the error of experiment. However, on calculating the 50° figures, where one would expect the experimental error to be, if anything, greater, the variation, with the exception of fraction 6, was much less, the values lying between 1·780 and 1·783. It is significant that fraction 6 was the only case where the liquid level was measured in the wider limb. If 6 is dropped from both series of measurements, the agreement of the 50° series is almost perfect and the results at 20° very irregular, without, however, showing a progression in either direction. In our opinion these variations in density are real and can be accounted for as follows: (*a*) intensive drying slows down the attainment of inner equilibrium at 20°, but not appreciably at 50°; (*b*) the equilibrium proportions at 20° and 50° differ considerably. Unless, therefore, a sample is cooled very slowly from 50° to 20°, its composition will be a function of its previous thermal history, and therefore the density will vary in an irregular manner. It is worthy of note that Schenck observed progressive volume changes with time at low temperatures.

Our mean values for 20° and 50° are in good agreement with the results of Lichty and Berthoud, but they are about 1 per cent. higher than Schenck's figures. Using our mean values we obtain for the coefficient of expansion of liquid sulphur trioxide the value 0·00256. This is very high, as was pointed out by Schenck, and is perhaps connected with the complex nature of the liquid.

Applying a similar method of consideration to the surface tension figures, we find that the 20° figures vary between 31·84 and 29·73, with a mean of 31·19, while the 50° figures vary between 24·99 and 26·16, with a mean of 25·62, *i.e.* at 20° there is a maximum deviation from the mean of — 4·65 per cent. and of — 2·45 per cent. at 50° where the experimental accuracy is certainly much less. If the latter deviation represents our experimental error, as it probably does at 50°, we have the similar behaviour to that of the densities. Again, there is no systematic drift, but this receives the same explanation as the densities. The most remarkable thing is that, at 20°, while Schenck's figure is 4 per cent. lower than that of Berthoud, our figure is 4·75 per cent. lower than Schenck's; at 50° Schenck is 3·15 per cent. lower than Berthoud, Campbell and Smith 7·7 per cent. lower than Schenck. It is significant that the conditions of Schenck's work approached those of intensive drying. The conditions of our work were such as to give high, rather than low, results, and therefore, if this further lowering is accepted as real, we are forced to conclude that intensive drying has lowered the surface tension of both pseudo-components. Briscoe, Peel and Robinson [12] carried out measurements similar to ours on intensively dried benzene. They found no significant change in density, but they did find a fall of 0·30 units in the surface tension of the liquid as a whole.

Using our mean values of surface tension at 20° and 50° we obtain for the Ramsay-Shields' constant the value 1·71. Substituting this value in the Ramsay-Shields-Eotvos equation gives a value of 245·2° for the critical temperature, but since the molecular surface energy is not a linear function of temperature for an associated liquid such as sulphur trioxide probably is, it is not surprising that the value deviates considerably from the experimental value of Schenck (216°).

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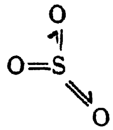
[12] Briscoe, Peel and Robinson, *J.C.S.*, 1929, 368.

The parachors at 20° and 50°, calculated from the final mean values and neglecting the density of the saturated vapour, have the following values:

$$P_{20^\circ} = 98{\cdot}5$$
$$P_{50^\circ} = 101$$

Sugden [5] quotes the calculated parachor of the simple unassociated molecule as 128·2, presumably from the formula



In other words, anomalies of — 29·7 and — 27·2 are exhibited at the two temperatures. This is explained by assuming association in the liquid. Now the formula given by Sugden (*cf.* p. 546) gives a parachor of 107 per 1/3 . S_3O_9 molecule, but undoubtedly there are present in the liquid other types of molecule (*e.g.* S_2O_6), giving parachor values differing from 107.

The melting-point ranges show the heterogeneous nature of the solidified liquids. At the same time reference to Smits' theory is hardly necessary to explain the facts here. The drastic chilling we were obliged to resort to, to produce solidification may simply have produced a mixture of α-, β-, and γ-forms. In order, however, that they may affect one another's melting-points, they must be able to retain their identity after fusion, and this again brings us back to Smits' theory, or something very like it.

Summary.

Sulphur trioxide was intensively dried for several months by passing its vapour through phosphorus pentoxide. The density and surface tension of successive fractions were determined. No change in the mean density was observed, but the density at 20° of successive fractions varied considerably, while the densities at 50° were practically invariable. Similar behaviour was observed with the surface tension. The surface tension of the whole was lowered distinctly below the figures of predecessors. This behaviour has been interpreted in the light of Smits' theory. The melting-point ranges of solidified α-sulphur trioxide have been determined and great heterogeneity demonstrated.

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ON THE ELECTROLYTIC SEPARATION OF THE HYDROGEN ISOTOPES ON A PALLADIUM CATHODE.

By Adalbert Farkas.

Received 8th January, 1937.

It was shown in a series of papers [1] that the electrolytic separation of the hydrogen isotopes might be due to several causes, and that, with certain assumptions, it was possible to deduce theoretical separation factors of the same order of magnitude as those observed experimentally. It was, however, not possible theoretically to decide with certainty what was the exact mechanism of the electrolytic separation in any particular case.

Obviously, in the electrolytic separation of the hydrogen isotopes, there are three different types of processes :- –

(*a*) Production of H and D atoms on the electrode.
(*b*) Exchange of H and D atoms between electrode and solution.
(*c*) Production of molecular gas.

The processes (*a*) and (*b*) take place at the interface electrode-solution, and (*c*) on the interface solution-electrode-gas.

Fowler [2] showed that, in steady electrolysis, no accumulation of substance can take place, and therefore the interchange of H and D atoms between the electrode and solution is of decisive importance. If this interchange is negligibly small, the separation is governed by the relative rate of production of H and D atoms (*e.g.*, by the discharge of $H^{\cdot}$ and $D^{\cdot}$ ions) on the electrode, whatever be the rate of formation of molecular gas. On the other hand, if complete equilibrium is established [3] between gas and solution by this exchange reaction and by the dissociation of molecular gas on the electrode, the separation factor becomes equal to the equilibrium constant of the reaction

$$H_2O + HD \rightleftharpoons HDO + H_2,$$

and the relative rates of production of H and D atoms and of their recombination to molecules on the electrode are irrelevant.

Halpern and Gross [4] recently made the assumption that in the electrolysis of a mixture of light and heavy water an initial intermediate equilibrium is set up between H and D atoms on the electrode and the solution, and they were able to show that, with reasonable rates of recombination of the atoms, a fairly large separation resulted.

The present experiments were carried out to obtain some information as to the speed of the exchange reaction involving atoms and, thus, as to the rôle of the intermediate equilibrium postulated by Halpern and Gross. For these experiments a palladium electrode seemed to be especially suitable for the following reason. Using a palladium cathode, the electrolysis can be so conducted that the hydrogen discharged at the cathode is quantitatively absorbed and the development of gas only sets in after the palladium has been saturated with hydrogen. A comparison of the D content of the occluded gas with that of the evolved gas should reveal whether an exchange reaction is operative or not: different D contents cannot be expected unless there is a sufficiently rapid exchange of H and D atoms between the solution and the electrode.

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[1] *E.g.*, H. C. Urey and G. K. Teal, *Rev. Mod. Physics*, 1935, 7, 41.
[2] R. H. Fowler, *Proc. Roy. Soc.*, *A*, 1934, 144, 452.
[3] A. and L. Farkas, *ibid.*, 146, 623 ; *J. Chem. Physics*, 1934, 2, 468.
[4] O. Halpern and Ph. Gross, *J. Chem. Physics*, 1935, 3, 452.

Anticipating the results, it may be stated that the present experiments are in substantial agreement with the mechanism proposed by Halpern and Gross.

Experimental.

The palladium was used in form of a foil (5 × 20 mm., 0·05 mm. thick). A simple method of making palladium ready to occlude hydrogen quantitatively in the electrolysis consists in oxidising it superficially by heating it up in air to red heat; the palladium then assumes a blue colour which, however, soon disappears when the electrolysis is started.

The electrolysis of the heavy water was carried out at 20° C. in a small U-tube as shown in Fig. 1. About 2 c.c. of the electrolyte were sufficient to fill the cell. The palladium-foil cathode was hung on a small hook of Pd wire, and could be readily removed. The gas from the cathode was driven out by heating it up to 320° C., at which temperature practically all the gas occluded in the palladium is given up in a few minutes. The amount of such occluded gas was equivalent to the coulombs passed through the cell if allowance were made for the hydrogen (a few hundredths of a cubic centimetre) used up for the reduction of the surface oxide. The cathode appeared to be saturated when approximately 500-600 volumes of hydrogen had been absorbed (the cathode was completely covered by the electrolyte). The gas given up (a few tenths of a cubic centimetre to a few cubic centimetres) by the cathode and that evolved in the electrolysis was analysed by the micro-thermo-conductivity method.[5]

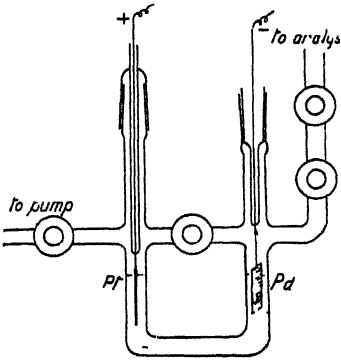

FIG. 1.—On the electrolytic separation of the hydrogen isotopes on a palladium cathode.

The charging of the palladium foil and the analysis of the occluded gas were repeated several times with the same foil and with different foils, at different currents and different states of saturation. The measurements were also repeated with different concentrations of heavy water and a comparison was made between the separation obtained in alkaline and acid solutions. In the acid solution the D content of the occluded gas was compared with that of the gas evolved in the electrolysis. Some typical results are summarised in Tables I., II. and III. The separation coefficients are expressed as $(H/D)_{\text{occl.}}/(H/D)_{\text{sol.}}$ and $(H/D)_{\text{evolv.}}/(H/D)_{\text{sol.}}$, $(H/D)_{\text{sol.}}$, $(H/D)_{\text{occl.}}$ and $(H/D)_{\text{evolv.}}$ being the relative concentration of hydrogen and deuterium in the solution, in the gas occluded in the palladium and in the gas evolved in the electrolysis respectively. From these results, the following points emerge:—

(1) The separation coefficient relative to the occluded gas is independent of the current density, the degree of saturation and the D content of

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[5] A. and L. Farkas, *Proc. Roy. Soc. A*, 1934, **144**, 467.

the electrolyte, and is practically the same in acid or alkaline solutions, its mean value being about 6·6.

(2) The separation coefficient relative to the gas evolved electrolytically is similarly independent of the experimental conditions, and has the mean value of 4·4.

TABLE I.—VARIATION OF THE CURRENT.

(Electrolyte: 26 per cent. D, 2 N H_2SO_4. Surface of the Cathode 2 cm^2. Occluded Gas = 0·2 c.c.)

Current in mA.	Per Cent. D in the—		Separation Coefficient Relative to—	
	Occluded Gas.	Evolved Gas.	Occluded Gas.	Evolved Gas.
2·5	4·9	7·5	6·8	4·3
10	4·9	—	6·8	—
40	5·2	7·6	6·4	4·3

TABLE II.—VARIATION OF THE DEGREE OF SATURATION OF THE CATHODE.

Electrolyte.	C.c. Occluded.	Per Cent. D in the Occluded Gas.	$(H/D)_{\text{occl.}}/(H/D)_{\text{sol.}}$
69 per cent. D 2N H_2SO_4 .	0·5	26·5	6·2
	2·6 (saturated)	26·2	6·2
52 per cent. D 2N H_2SO_4 .	0·2	14·2	6·6
	2·5	12·8	7·4
	(saturated) 2·5	13·8	6·7

TABLE III.—VARIATION OF D-CONTENT IN THE ELECTROLYTE.

Electrolyte.		Per Cent. D in the—		$\dfrac{(H/D)_{\text{occl.}}}{(H/D)_{\text{sol.}}}$.	$\dfrac{(H/D)_{\text{evolv.}}}{(H/D)_{\text{sol.}}}$.
	Per Cent. D.	Occluded Gas.	Evolved Gas.		
2N H_2SO_4 .	26	5·0	7·5	6·6	4·3
,, .	52	14	21	6·6	4·1
,, .	69	26	32	6·3	4·7
0·1N NaOH .	75	31	—	6·7	—

If the palladium cathode is saturated, the evolution of gas at the cathode also continues, even after the current has been stopped. The D content of this gas and of that given up by the saturated cathode in vacuo at room temperature was compared with that evolved in the electrolysis and found to be nearly the same (see Table IV.).

TABLE IV.—ELECTROLYTE 52 PER CENT. D, 2N H_2SO_4.

Gas.	Per Cent. D.
Evolved at 28 mA	21·0
Bubbling after electrolysis stopped	20·1
Given up in vacuo at 20° . .	20·8

To obtain some information as to the exchange reactions occurring at the electrode, the following experiments were carried out :—

(*a*) The cathode was saturated with pure H_2 and placed into an acid solution containing 69 per cent. D. The gas bubbling through the solution was found to contain not more than 0·1 per cent. D.

(*b*) Similar results were obtained with a palladium disc sealed into glass and brought into contact on one side with acidulated ordinary water and on the other side with heavy water (39 per cent. D). If hydrogen was fed electrolytically from the ordinary water side to the palladium disc, the hydrogen bubbling through heavy water at a rate of a few mm.^{3}/minute did not contain more than 0·1 per cent. D.

(*c*) If a few tenths of a cubic centimetre of ordinary hydrogen were brought into contact with the electrolyte containing heavy water in the cell, the establishment of the equilibrium $H_2 + HDO \rightleftharpoons HD + H_2O$ through the catalytic activity of the freshly reduced cathode took several hours. Since the same amount of gas is evolved in the electrolysis within a few minutes, the exchange reaction involving molecular hydrogen proceeds negligibly slowly.

Discussion.

The first question for discussion concerns the difference in the D content of the hydrogen occluded in the palladium and of the evolved gas. There are two possible explanations for this behaviour: (*a*) The relative rate of production of H and D atoms in the electrolysis changes with the degree of saturation of the cathode; (*b*) There is an interchange of H and D atoms between the electrode and the solution.

For the first explanation, we must assume that until the palladium contains no gas, or only a little, H atoms are produced with, say, 6·6 times larger probability than D atoms but, as the palladium becomes more and more saturated, this ratio diminishes to about 4·4. Consequently, we should expect more deuterium in the palladium the more saturated it is. As shown in Table II., however, the D content is independent of the degree of saturation and, therefore, this explanation must be rejected.

On the other hand, the second explanation is consistent with experimental facts. The exchange reaction balances the production of atoms, the occlusion of atoms and the formation of molecules by interchange of H atoms for D atoms (or vice versa) on the surface of the electrode. The assumption of an exchange reaction is necessary, since this reaction has to dispose of the superfluous number of H or D atoms resulting from their different speed of recombination.

We must distinguish between two different types of such exchange reactions, depending on whether the interchange process is associated with the deposition of atoms on the electrode from the solution at the interface solution/electrode or with the formation of molecules at the interface solution/electrode/gas. The latter process occurs in the catalytic exchange reaction between water and molecular hydrogen discovered and investigated by Horiuti and Polanyi.[6] This type of exchange reaction proceeds, however, far too slowly on tho palladium cathode compared with the rate of production of molecular hydrogen in the electrolysis, since it took several hours to establish equilibrium between heavy water and a few tenths of a cubic centimetre of hydrogen, whereas this small amount of gas, as has been said, is produced in the electrolysis within a few minutes (see above). We must, therefore, conclude that the effective exchange reaction takes place between the electrode and solution, and may be written schematically[7] as

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[6] J. Horiuti and M. Polanyi, *Mem. Proc. Manchester Lit. Phil. Soc.*, 1934, 78, 47.

$$MH + HDO \rightleftharpoons MD + H_2O \quad . \quad . \quad . \quad (1)$$

M being the electrode. Such an exchange reaction has not as yet been investigated, but it can probably be regarded as being involved in the first kind of exchange as the second step towards the dissociation of molecular hydrogen

$$H_2 + 2M \rightleftharpoons 2MH \quad . \quad . \quad . \quad . \quad (2)$$

It was shown previously[8] that in the presence of water on a platinum catalyst (or on an enzyme) the rate of the *para*-hydrogen conversion is about the same as the rate of exchange with heavy hydrogen. Since the same behaviour may be expected to be shown on a palladium surface reaction (1) will be much more rapid than reaction (2). We will assume, with Halpern and Gross, that the velocity of this reaction is so large that the equilibrium (1) is completely established, and furthermore that the relative concentrations of H and D atoms are the same inside the palladium as on the surface of the cathode. This assumption of the complete establishment of the equilibrium (1) seems justified, since the D content of the gas occluded in the palladium is independent of the current density, and the degree of saturation and remains unchanged whether the electrolysis is carried out in acid or alkaline solutions (see Tables I., II. and III.).

The complete equilibrium in the system palladium-solution-gas is, however, not settled through the establishment of the equilibrium $MH + HDO \rightleftharpoons H_2O + MD$. According to the given scheme, the processes necessary for the attainment of complete equilibrium are :—

$$\begin{aligned} 2MH &\rightleftharpoons 2M + H_2 \quad . \quad . \quad . \quad (2a) \\ MH + MD &\rightleftharpoons 2M + HD \quad . \quad . \quad . \quad (2b) \\ 2MD &\rightleftharpoons 2M + D_2 \quad . \quad . \quad . \quad (2c) \end{aligned}$$

These processes, however, are not reversible in the present experiments, and proceed preferentially from the left to the right.

The exchange reaction on the interface solution-electrode-gas is also absent when hydrogen occluded in the palladium leaves the electrode to form molecular hydrogen : the D content of the gas, bubbling through heavy water, leaving the cathode previously saturated with H_2 was found to be not more than 0·1 per cent. This behaviour is, at first glance, somewhat unexpected, since one would have thought that the hydrogen is present within and on the surface of the palladium, in atomic form and, thus, has just as good a chance for an exchange reaction as the atoms produced in the electrolysis. Closer consideration shows, however, that the position of the atoms coming from the interior of the electrode and of those deposited from the solution is not entirely symmetrical. Whereas the atoms from the solution are deposited on the very surface of the electrode and have ample chance to come into contact with water, the atoms coming from the interior will reach the surface in internal cracks and the formation of gas bubbles will soon prevent contact with water.

The lack of the exchange reaction associated with the evolution of gaseous hydrogen is once more evident from the fact that on electrolysis of heavy water, the same D content is found (see Table IV.) whether (*a*) in the gas evolved on the cathode during the electrolysis, or (*b*) in the gas given up by the saturated cathode as soon as the electrolysis is stopped, or (*c*) in the gas given up by the saturated cathode in vacuo at room temperatures.

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[7] This reaction may involve ionisation.

[8] A. Farkas, *Trans. Faraday Soc.*, 1936, **32**, 922.

These experiments lead to another important point. The composition of the hydrogen leaving the saturated electrode at room temperature is different from that of the gas occluded by the electrode, owing to the different rates of recombination of hydrogen and deuterium atoms.

If we denote by λ_{11}, λ_{12} and λ_{22} the respective recombination constants, for the formation of the molecules H_2, HD and D_2, and assume

$$\lambda_{12}{}^2/\lambda_{11}\lambda_{22} = 4,$$

we obtain

$$\left(\frac{\lambda_{11}}{\lambda_{22}}\right)^{\frac{1}{2}} = \frac{(H/D)_{\text{evap.}}}{(H/D)_{\text{occl.}}} = 0{\cdot}63.$$

This means that the D atoms leave the surface more readily by forming molecules than the H atoms, a result which is readily explained as follows: From the experiments of Melville and Rideal,[9] and Sieverts and Zapf,[10] we know that the heat of absorption in Pd is less for D_2 than for H_2, consequently the separation of the energy levels of H and D in the palladium will be less than that of the levels of $\frac{1}{2}H_2$ and $\frac{1}{2}D_2$ in the gas phase. If there is an energy of activation for dissociation of molecular hydrogen on the palladium it will be reasonable to assume that in general the separation of the levels in the activated state will be somewhere half-way between that in the absorbed state and in the free gaseous state. The energy of activation for the recombination will therefore be less for D atoms than for H atoms.

It is interesting to note that we can, from the present experiments, determine the numerical values of two quantities of decisive importance which appear in the formula given by Halpern and Gross for the electrolytic separation coefficient. According to these authors, the concentration of the H and D atoms on the electrode in equilibrium with the solution is given by

$$(H/D)_{\text{electr.}} = \frac{k_H}{k_D}\left(\frac{K_{11}}{K_{22}}\right)^{\frac{1}{2}} K(H/D)_{\text{sol.}}$$

(where k_H/k_D is the ratio of the distribution coefficients of H and D atoms between gas and electrode), and the separation coefficient by

$$\alpha = (H/D)_{\text{evolv.}}/(H/D)_{\text{sol.}} = \left(\frac{\lambda_{11}}{\lambda_{22}}\right)^{\frac{1}{2}} (H/D)_{\text{electr.}}/(H/D)_{\text{sol.}}.$$

In this expression we know the ratio of the dissociation constants of H_2 and D_2 at 20° C.[11]

$$K_{11}/K_{22} = 14,$$

and K the equilibrium constant of the reaction

$$HD + H_2O = H_2 + HDO$$

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[9] H. W. Melville and E. K. Rideal, *Proc. Roy. Soc., A*, 1935-36, **153**, 91.

[10] A. Sieverts and G. Zapf, *Z. physik. chemie, A*, 1935, **174**, 359.

[11] Johnston and Long, *J. Chem. Physics*, 1934, **2**, 389; Giauque, *J. Amer. Chem. Soc.*, 1930, **52**, 4816.

$K = 3{\cdot}5$ (being the mean value from the experiments of Bonhoeffer and Rummel [12] and Farkas and Farkas [13]), and therefore

$$\alpha = 13{\cdot}1 \frac{k_H}{k_D}\left(\frac{\lambda_{11}}{\lambda_{22}}\right)^{\frac{1}{2}}.$$

The relative rate of recombination of H and D atoms is

$$(\lambda_{11}/\lambda_{22})^{\frac{1}{2}} = (H/D)_{\text{evolv.}}/(H/D)_{\text{electr.}} = (H/D)_{\text{evolv.}}/(H/D)_{\text{occlud.}},$$

and we again obtain

$$\left(\frac{\lambda_{11}}{\lambda_{22}}\right)^{\frac{1}{2}} = 0{\cdot}63.$$

The ratio of the distribution coefficients of the H and D atoms between gas and the electrode is

$$\frac{k_H}{k_D} = (H/D)_{\text{electr.}}(D/H)_{\text{sol.}} \cdot \frac{1}{13{\cdot}1} = 0{\cdot}5.$$

This value is in good agreement with one which can be deduced from solubility measurements. According to Sieverts and Zapf (extrapolated value) the relative solubilities of hydrogen and deuterium in palladium at 20° C. is $L_{H_2}/L_{D_2} = 3$. Since

$$(L_{H_2}/L_{D_2})^{\frac{1}{2}} = \frac{k_H}{k_D} \cdot \left(\frac{K_{11}}{K_{22}}\right)^{\frac{1}{2}}.$$

$$K_H/k_D = 0{\cdot}46.$$

The agreement with the value of 0·5 can be regarded as satisfactory, and as a further support for the mechanism proposed by Halpern and Gross.

Summarising the results, we picture the following mechanism for the electrolytic separation of the hydrogen isotopes on a palladium cathode.

The deposition of the H and D atoms from the solution on the electrode by the current is followed by a rapid exchange of H and D atoms between electrode and solution, whereby the relative concentration of these atoms on the electrode corresponds to the equilibrium

$$\text{MH} + \text{HDO} \rightleftharpoons \text{MD} + \text{H}_2\text{O}.$$

From this equilibrium layer the atoms recombine to form molecules, the relative rate of formation of the molecules H_2, HD and D_2 being of decisive importance for the efficiency of the electrolytic separation.

Finally, we have to consider how far the conclusions reached, under the present experimental conditions, in the study of the electrolysis on palladium can be generalised. The establishment of the intermediate equilibrium will be maintained so long as the exchange reaction can keep pace with the evolution of hydrogen. Let n be the rate of production of atoms, c the concentration on the electrode, λ and k the velocity constants for recombination and for exchange respectively, then

$$n = \lambda c^2,$$

and the rate of exchange $= kc,$

or the equilibrium continues until

$$\frac{k^2}{\lambda} > n,$$

i.e. the equilibrium is maintained even at high rates of hydrogen evolution provided the recombination constant is small enough. For the quantitative investigation of this question of the experiments must be extended to higher current densities.

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[12] K. F. Bonhoeffer and K. W. Rummel, *Naturwiss.*, 1933, **22**, 45; K. F. Bonhoeffer, *Z. Elektrochemie*, 1934, **40**, 469.

[13] A. and L. Farkas, *Trans. Faraday Soc.*, 1934, **30**, 1071.

The absolute value of the separation coefficient is given by the formula of Halpern and Gross,

$$\alpha = 13{\cdot}1\,\frac{k_{\mathrm{H}}}{k_{\mathrm{D}}}\cdot\left(\frac{\lambda_{11}}{\lambda_{22}}\right)^{\frac{1}{2}}.$$

We put approximately $k_{\mathrm{H}}/k_{\mathrm{D}} \propto e^{-(E_1{}^{\circ} - E_2{}^{\circ})RT}$

and $(\lambda_{11}/\lambda_{12})^{\frac{1}{2}} \propto e^{-(E_1{}^{\circ\prime} - E_1{}^{\circ} - E_2{}^{\circ\prime} + E_2{}^{\circ})/RT}$

(E° = zero point energy in the absorbed state, $E^{\circ\prime}$ = zero point energy in the activated state).

Therefore $k_{\mathrm{H}}/k_{\mathrm{D}}\cdot\left(\frac{\lambda_{11}}{\lambda_{22}}\right)^{\frac{1}{2}} \propto e^{-(E_1{}^{\circ\prime} - E_2{}^{\circ\prime})/RT}.$

The product of these two decisive terms will, therefore, depend mainly on the separation of the energy levels in the activated state involved in the recombination. We can distinguish two limiting cases: (*a*) The separation is negligible; (*b*) The energy of activation for dissociation is negligible. In the former case the separation factor will be about 12. In the latter case the activated state will be identical with the final state, *viz.*, with that of molecular hydrogen, and the separation factor becomes 3·5, the equilibrium constant of the reaction

$$\mathrm{HD} + \mathrm{H_2O} = \mathrm{H_2} + \mathrm{HDO}.$$

Under these conditions, complete equilibrium is established between solution, electrode and gas.

The present experiments will be extended to investigate the electrolytic separation on all metals which take up sufficient amounts of hydrogen such as iron, nickel, platinum, tantal, etc.

Summary.

Using a palladium cathode, the electrolysis of mixtures of light and heavy water has been carried out in alkaline and acid solutions. The D content of the evolved gas has been compared with that of the gas occluded in the cathode and the following separation factors found

$$\frac{(H/D)_{\mathrm{occl.}}}{(H/D)_{\mathrm{sol.}}} = 6{\cdot}6, \qquad \frac{(H/D)_{\mathrm{evolv.}}}{(H/D)_{\mathrm{sol.}}} = 4{\cdot}4.$$

It is shown that the separation factor 6·6 can be regarded as caused by the establishment of the equilibrium

$$\mathrm{MH} + \mathrm{HDO} = \mathrm{MD} + \mathrm{H_2O}$$

on the electrode (M), in agreement with the theory proposed by Halpern and Gross. On the other hand, the difference in the separation factors 6·6 and 4·4 is to be attributed to a different rate of recombination of H and D atoms on the palladium.

The present experiments were carried out in the Department of Colloid Science of Cambridge University and written up for publication in July, 1936. The publication, however, was delayed for reasons over which the author had no control.

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TRANSPORT OF IONS IN PRESENCE OF COLLOIDS.

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Several investigations have been made of the apparent mobilities of ions in the presence of colloids: for example that of K˙ in stannic acid sols [1] and that of Cl′ in iron oxide sols.[2] Many other such mobilities have also been determined in an indirect manner.[3] But, so far as I am aware, in all cases the ion under investigation was present during the formation of the sol and was undoubtedly a constituent of the colloid particle.* It is, therefore, impossible to derive from these measurements any information concerning the influence of the particle upon the movement of the surrounding ions. The theory of the diffuse double layer predicts the existence of such an influence, and even allows it to be calculated in the case of large rod-shaped particles, when the effect may be regarded as the inverse of the influence of membranes upon ionic mobilities.

As an example of a system where the inclusion of the ion in the colloid particle seems unlikely, I have investigated an As_2S_3 sol to which some ammonium chloride was added, and have compared the apparent mobility of $NH_4^{\cdot}$ in this system with that in an equally concentrated NH_4Cl solution. A strong retardation of $NH_4^{\cdot}$ by As_2S_3 particles was found. Its magnitude does not contradict the theory, but cannot be claimed as conclusive evidence in its favour as the conception of exchange adsorption is also consistent with the experimental results.

Measurements.

The measured quantities were as follows :—

(1) The electrical conductivity of the sol, the sol—NH_4Cl mixtures, and the NH_4Cl solutions at 20°.

The conductivity of the sol with and without NH_4Cl increased when kept in the conductivity cell with platinized electrodes; the lowest values were accepted as correct. The conductivity of the water used ($2 - 5 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$) was not subtracted.

(2) The mobilities of $NH_4^{\cdot}$ and of As_2S_3 at 20°. These were measured in the simple apparatus of Henry and Brittain.[4]

Ammonium was determined in the original solution and, after the transport experiment, in the cathodic and the anodic solutions by adding alkali and distilling the ammonia into 0·02 *N* H_2SO_4; methyl red was used as indicator.†

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[1] R. Wintgen, *Z. physik. Chem.*, 1922, **103**, 238.

[2] R. Wintgen and M. Biltz, *ibid.*, 1923, **107**, 403.

[3] C. Robinson, *Trans. Faraday Soc.*, 1935, **31**, 245; G. S. Hartley, B. Collie and C. S. Samis, *ibid.*, 1936, **32**, 795, etc.

* *I.e.* was not merely adsorbed on its surface but formed a part of its structure. For example, many workers admit that a part of Cl in iron oxide sols is present in the particles as FeOCl; it is clear that the average mobility of Cl in these sols is different from that of Cl ions.

[4] D. C. Henry and J. Brittain, *Trans. Faraday Soc.*, 1933, **29**, 798.

† The preliminary analyses were executed by Mr. D. Entwistle.

Arsenic trisulphide was determined by weighing as such.

(3) The " total charge " on the particles in 1 c.c. of the sol.

50 c.c. of the sol was precipitated on the steam-bath with about 2 gm. (weighed to 0·001 gm.) of 0·149 *N* $N(CH_3)_4Cl$ and filtered through a double paper filter; the precipitate was washed on the filter until the volume of filtrate reached 100·0 c.c. It was proved in every case that all subsequent portions of the wash water were neutral. A mixture of 2 gm. of 0·149 *N* $N(CH_3)_4Cl$ and 50 c.c. water was filtered, and the filter washed in the same manner. The concentrations of $N(CH_3)_4^{\cdot}$ in both filtrates were determined as previously described.[5] I used $N(CH_3)_4Cl$ rather than $BaCl_2$ or any similar salt since Ba, Sr, etc., may give insoluble salts with the products of oxidation or hydrolysis of arsenic trisulphide,* while tetramethylammonium compounds of all relevant anions are easily soluble.

A part of the filtrate was titrated with 0·02 *N* NaOH in the presence of methyl red.

The sols were employed without previous dialysis. The sol used in the final series contained 7·01 gm./l. As_2S_3.

Results.

The chief results are given in the table below. κ is the specific conductivity, u and v the mobilities of As_2S_3 and $NH_4^{\cdot}$. The values of v for the solutions IV. and V. are almost 4 per cent. less than the recorded ones; † as, however, the error is obviously a systematic one it does not affect the comparison of the mobilities with and without colloid. Apart from this error the values of v should be correct within 1 per cent. for the solutions IV. and V., within 2 per cent. for solution III., and within 3 per cent. for solution II.

Solution.	$\kappa \, . \, 10^4$ ohm.$^{-1}$ cm.$^{-1}$.	$v \, . \, 10^4$ cm./sec.	$u \, . \, 10^4$ per volt./cm.	Number of Experiments.
I. As_2S_3	1·14	—	−6·6*	1†
II. $As_2S_3 + 1{\cdot}73 \times 10^{-3}$ *N* NH_4Cl	3·98	5·23	−4·08	5†
III. $As_2S_3 + 4{\cdot}41 \times 10^{-3}$ *N* NH_4Cl	7·56	5·70	−3·77	3†
IV. $1{\cdot}75 \times 10^{-3}$ *N* NH_4Cl	$2{\cdot}39_5$	6·58	—	5
V. $4{\cdot}38 \times 10^{-3}$ *N* NH_4Cl	5·90	6·54	—	3

* This value is taken from my paper in *Trans. Faraday Soc.*, 1936, **32**, 1648; in which work the same sol was used as that which served for preliminary experiments described in this paper.

† Only the final series is taken into account.

The amount of $H^{\cdot}$ found in the filtrate after the coagulation with $N(CH_3)_4Cl$ was $7{\cdot}2 \times 10^{-4}$ gm.-mol./l. of the original sol. A previous addition of KCl (0·6 c.c. of 0·4 *N* KCl per 50 c.c. of the sol) scarcely affected this value.‡

The amount of $N(CH_3)_4^{\cdot}$ " adsorbed " by As_2S_3 precipitate was $5{\cdot}9 \, . \, 10^{-4}$ gm.-mol./l. of the original sol or 0·84 gm.-mol./gm. of As_2S_3. The " colloid equivalent " of the As_2S_3 was accordingly 49.

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[5] J. J. Bikerman, *Z. analyt. Chem.*, 1932, **90**, 335.

* See, for instance, the discussion of Kargin and Klimovitzkaja, *Acta physicochimica*, 1935, **1**, 729.

† *Cf.* the error of the results of Wintgen and Biltz[2] who determined the transport number of Cl' in NaCl.

‡ In the theory of diffuse double layer the total charge depends on the ionic concentration of the intermicellar liquid.

Discussion.

(*a*) From the Point of View of Exchange Adsorption.

Ammonium ions adsorbed by arsenic trisulphide particles possess the mobility u of the particles. If the mobility of free $NH_4^{\cdot}$ be denoted by v_c, the average mobility by v, and the adsorbed fraction by x, we have

$$v = ux + v_c(1 - x).$$

For the solutions II. and III. we obtain thus $x = 0{\cdot}13$ and $x = 0{\cdot}082$; the amount adsorbed by 1 litre of sol would be, accordingly, $2{\cdot}2 \times 10^{-4}$ and $3{\cdot}6 \times 10^{-4}$ gm.-mol. $NH_4^{\cdot}$.

On the other hand, the replacement of $2{\cdot}2$ or $3{\cdot}6 \times 10^{-4}$ gm.-mol. $NH_4^{\cdot}$ in the solution by the equivalent amount of $H^{\cdot}$ would increase the conductivity by $2{\cdot}2 \times 10^{-7}\,(324\text{-}66) = 0{\cdot}57 \times 10^{-4}$ or by $3{\cdot}6 \times 10^{-7}$ $(322\text{-}66) = 0{\cdot}92 \times 10^{-4}$. The table shows that the conductivity of the mixtures II. and III. exceeded the sum of the single conductivities by $0{\cdot}47 \times 10^{-4}$ and $0{\cdot}48 \times 10^{-4}$. The agreement of the figures 0·57 and 0·47 is satisfactory but the discrepancy of the figures for the solution III. shows, that the simple picture we have made is not yet complete.

Weiser and Gray [6] determined the displacement of $H^{\cdot}$ by $NH_4^{\cdot}$ on similar As_2S_3 particles potentiometrically. Assuming the adsorbed amount to be proportional to the arsenic trisulphide concentration I calculate for a sol of 7 gm./l. and NH_4Cl concentrations of 1·73 and $4{\cdot}41 \times 10^{-3}$ N displacements amounting to $1{\cdot}2 \times 10^{-4}$ and $1{\cdot}6 \times 10^{-4}$ gm.-mol. NH_4 per l. of sol.[*]

(*b*) From the Point of View of Gouy's Theory.

Colloid particles, when moving in electric field, carry with them some intermicellar liquid; an equal volume of liquid moves at the same time in the opposite direction between the particles so that no net transport of solvent occurs. If V_1 be the volume of the particle, $V_2 = V_1 +$ the volume of liquid moving in the same direction as the particle, and $V_3 = V_2 +$ the volume of liquid moving in the opposite direction round one particle, we have

$$\int_{V_1}^{V_2} UX\,dV = \int_{V_2}^{V_3} UX\,dV,$$

U being the velocity of the liquid relatively to the vessel, and X the field strength which also depends on the distance from the particle. If the distribution of ions in the liquid were uniform the streaming of the solvent would not affect the average ionic mobility. But the immediate surroundings of a negative particle (for example) contain more cations than an equal volume at a distance from any particle; more cations will accordingly be transferred with the solvent to the anode than to the cathode, and the average mobility of the cation will be reduced.

If the distance between the particles is large enough the cation concentration C in the liquid moving towards cathode will be practically constant within the whole volume $V_3 - V_2$, and the transported amount of cations will be $C\int_{V_2}^{V_3} UX\mathrm{d}V$. Within the volume $V_2 - V_1$ the concentration is a function of the distance from the particle and equal to N_cC, where N_c is a function of the distance. The transported amount is $C\int_{V_1}^{V_2} N_cUX\mathrm{d}V$, and the net transport to the anode is $C\int_{V_1}^{V_2}(N_c - 1)UX\mathrm{d}V$.

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[6] H. B. Weiser and G. R. Gray, *J. physic. Chem.*, 1932, **36**, 2796.

[*] My final sol was exhausted before potentiometric measurements could be made.

The average mobility v is connected with the mobility, v_c, in the absence of colloid, the bulk concentration C_m, the number of particles, n, per c.c., and the macroscopic field strength X_0 according to the equation

$$C_m vX_0 = C_m v_c X_0 - nCX_1\int_{V_1}^{V_2}(N_c - 1)U\mathrm{d}V,$$

or

$$v - v_c = n\frac{CX_1}{C_m X_0}\int_{V_2}^{V_1}(N_c - 1)U\mathrm{d}V. \qquad . \quad . \quad (2)$$

X_1 is the average field strength within the "double layer."

As stated in the introduction the integral can only be evaluated for large rod-shaped particles. Eqns. (8) and (9) of a previous paper[7] —which may be consulted for the elucidation of this section—give:

$$\int_{V_1}^{V_2}(N_c - 1)U\mathrm{d}V = \Omega\frac{\sqrt{(DRT)^3}}{(\nu F)^2\eta\pi\sqrt{8\pi C}}\left(\frac{A+1}{A-1}\ln\frac{A+1}{A-1} - \frac{2}{A-1}\right)^* \quad (3)$$

where Ω is the surface of the particle, ν the valency of the ions, F the Faraday constant, η the viscosity, D the dielectric constant, and

$$A = \frac{e^{-\nu F\zeta/2RT} + 1}{e^{-\nu F\zeta/2RT} - 1},$$

ζ being the electrokinetic potential difference. Its value may be derived from the formula[8]

$$u = \frac{X_1}{X_0}\cdot\frac{D\zeta}{4\pi\eta}. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Unfortunately it is still impossible to calculate the fraction X_1/X_0 for small particles. If, however, we set $X_1 = X_0$ in eqn. (4) and $CX_1 = C_mX_0$ in eqn. (2) the errors thus caused will partially counterbalance each other. For solutions II. and III. this leads to the values $\zeta = 0{\cdot}057$ and $\zeta = 0{\cdot}053$ volt, corresponding to $A = 1{\cdot}95$ and $A = 2{\cdot}06$. Introducing these figures into eqn. (3) its righthand term becomes $2{\cdot}26 \times 10^{-7}n\Omega$ and $1{\cdot}18 \times 10^{-7}n\Omega$. The values of v being $0{\cdot}157$ and $0{\cdot}171$ while $v_c = 0{\cdot}197$ and $0{\cdot}196$ (in C.G.S. units) we obtain for $n\Omega$, that is the total surface of the particles in 1 c.c. of sol, the values $1{\cdot}8 \times 10^5$ sq. cm. and $2{\cdot}1 \times 10^5$ sq. cm. The agreement of these two figures is satisfactory but the absolute magnitude is improbably high. They would, for instance, give for the total charge of the particles per 1 c.c. of sol, according to eqn. (6) of the previous paper,[7] the values 10^{-6} and $1{\cdot}9 \times 10^{-6}$ gm.-equiv., which is considerably higher than either the

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[7] J. J. Bikerman, *J. chimie physique*, 1935, **32**, 460.

* A more complete expression in the brackets is

$$\frac{A+1}{A-1}\ln\frac{A+1}{A-1} - \frac{2}{A-1} + \frac{8}{\alpha l(A-1)}\left(\frac{1}{A} + \frac{1}{3^2A^3} + \dots\right),$$

where l denotes the distance between two particles and $1/\alpha$ the "thickness" of the "double layer."

[8] J. J. Bikerman, *Z. physik. Chem.*, *A*, 1934, **171**, 209.

"total charge" as determined by coagulation with $N(CH_3)_4Cl$ or the charge which would correspond with the conductivity of the sol or its mixtures.

There is no need, however, to abandon the theory on this account. If $n\Omega$ is of the order of 10^5 sq. cm. the particles must be very small, so small indeed that their velocity is expressed by the formula[9]

$$u = \frac{X_1}{X_0} \cdot \frac{D\zeta}{6\pi\eta} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

rather than by eqn. (4). Then ζ of solutions II. and III. becomes 0·085 and 0·080 volt, and we obtain for $n\Omega$ the value $0{\cdot}6 \times 10^5$ sq. cm. which is quite reasonable. But even that is only the upper limit[*] of $n\Omega$. All the theoretical formulæ employed have, as usual, been derived on the assumption that the particles have a simple (ellipsoidal) shape and a smooth surface. Any irregularity of form or roughness of surface will cause: (*a*) a reduction of the mobility—so that eqns. (4) or (5) yield too small values for ζ—and (*b*) an increased forced transport of ions with the particle.

It is possible, of course, that the observed effects are due partly to the exchange adsorption and partly to the diffuse double layer. New experiments are necessary in order to decide this question.

Summary.

The mobility of ammonium ions in presence of colloidal arsenic trisulphide has been measured. The observed retardation has been discussed from the points of view both of exchange adsorption and of the diffuse double layer.

I am indebted to Mr. D. C. Henry for hospitality and help and to the Professional Committee for German Jewish Refugees for a maintenance grant.

The Thomas Graham Colloid Research Laboratory,
University of Manchester.

[9] D. C. Henry, *Proc. Roy. Soc.*, *A*, 1931, **133**, 106.

[*] Similarly the theoretical values for the surface conductivity are always smaller than the experimental ones; see, for instance, J. J. Bikerman, *Koll. Z.*, 1935, **72**, 100.

THE STRUCTURE OF ELECTRODEPOSITED NICKEL.

By G. I. Finch and A. L. Williams.

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Crystal size and orientation in an electrodeposited metal are often determined by those of the substrate metal crystals. Thus Thomson[1] found that silver electrodeposited on a single crystal of copper itself formed a single crystal of normal lattice dimensions with an orientation similar to that of the substrate; and experiments carried out in this

[1] G. P. Thomson, *Proc. Roy. Soc.*, *A*, 1931, **113**, 1.

laboratory [2] have led to the discovery of numerous examples of similar effects which suffice to show clearly how strong these substrate influences are, at least in the initial layers of the deposit, even though the conditions of deposition are such as would otherwise normally lead to quite a different crystal size and orientation. Thomson did not determine the deposit thickness through which the substrate influence persisted, but Finch and Sun [2] working with polycrystalline substrates of sub-microscopic or microscopic crystal size found that, on approaching a film thickness of 10^3 A, the substrate influence showed signs of weakening, to vanish completely at less than 2×10^3 A, even in the most persistent case then studied (nickel on gold). Nevertheless, other workers, notably Hothersall,[3] using micrographical methods have in certain cases detected a substrate influence on the micro-structure persisting throughout electrodeposits of thicknesses exceeding as much as 0·5 mm. Hothersall's remarkable microphotographs afford such convincing proof of the continuation of microscopically visible substrate features throughout the deposit as to suggest that substrate crystal size and orientation were likewise preserved. Such a conclusion conflicts with the results obtained by Finch and Sun; [2] substrate crystal size and deposition conditions, however, differed widely in the two cases, and it is possible that such differences might well affect the depth of the deposit throughout which the substrate influence is propagated. The following experiments were undertaken in order to examine this question and, in particular, to ascertain to what extent similarity in micro-structure could be regarded as evidence of similarity in crystal size and orientation and possibly, as has sometimes been suggested,[4] of a lattice distortion, *i.e.*, a change in the characteristic lattice dimensions of the deposit crystals enforced by the substrate.

Experimental.

We have confined ourselves in these experiments to a study of the influence of copper and cuprous oxide substrates on electrodeposited nickel. Copper was available in the form of 15 mm. diameter discs assaying 99·95 per cent. Cu and 0·02 per cent. O_2. Three main series of experiments were carried out. In the first, in order to determine the effect of the electrodeposition conditions upon the orientation normally taken up by the deposit crystals in the absence of a specific substrate influence, some disc surfaces were highly polished and others prepared by vigorous criss-cross abrasion with fine (Hubert 000) emery paper, followed by a light cyanide etching to remove any Beilby layer formed. The electron diffraction reflection patterns from the etched surfaces consisted of continuous semicircles, and were thus characteristic of unorientated copper crystals of submicroscopic, or nearly so, dimensions. The polished surfaces gave the halo patterns characteristic of the Beilby layer.

For the second series, substrates with crystals of, for the most part, macroscopic dimensions, *i.e.*, a grain size with an exposed area of the order of 0·01 mm.^{2}, were obtained by heating copper discs in air at about 1000°, followed by annealing at 500° and quenching in water, the primary object of this "water-quench cycle" having been originally to obtain specimens suitable for a study of the copper-cuprous oxide rectifier. After removal of the oxide layers by sodium cyanide etching, the surfaces of the discs exhibited under the microscope a network of shallow depressions left behind by the cuprous oxide crystals, together with another network of sharply defined boundaries of what appeared to be relatively large copper crystals (Fig. 1); an impression confirmed by diffraction patterns of which Fig. 4 is typical.

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[2] G. I. Finch and C. H. Sun, *Trans. Faraday Soc.*, 1936, **32**, 852.

[3] A. W. Hothersall, *ibid.*, 1935, **31**, 1242.

[4] W. A. Wood, *ibid.*, 1935, **31**, 1248.

In the final series of experiments, cuprous oxide surfaces, prepared by the " water-quench cycle " followed by a cyanide etch sufficient to detach the cupric oxide skin, were used as substrates. Here again, both microscope and electron diffraction camera showed clearly that the cuprous oxide surface was macrocrystalline. The reflection patterns consisted of elongated spots, and were thus similar in type to Fig. 4. Cuprous oxide flakes mechanically detached from the copper matrix afforded remarkably clear transmission spot patterns characteristic of single crystal structure, thus fully confirming the macrocrystalline nature of the cuprous oxide substrates. A step-wise etching of the cuprous oxide layer with citric acid and light brushing with a camel hair brush to remove copper deposited in the process, combined with electron diffraction and microscopical examination at each stage, showed that the individual cuprous oxide crystals were columnar throughout.

Nickel was electrodeposited at 45° from the baths

$$(240 \text{ g. } NiSO_4 + 30 \text{ g. } H_3BO_3)/l \text{ (" strong bath "),}$$

and

$$(30 \text{ g. } NiSO_4 + 30 \text{ g. } H_3BO_3)/l \text{ (" weak bath ").}$$

The current densities were 0·3, 0·6 and 1·2 A/dcm.^{2}, corresponding to deposit thickness increases of 500, 1000 and 2000 A/min. respectively, estimates which were confirmed by direct weighing in the case of some of the thicker deposits.

The procedure followed may be summarised as follows. Except in the first series, where the nickel deposit surface alone was examined and then as a rule only by electron diffraction, the copper or cupric oxide substrate was microphotographed and its diffraction pattern recorded prior to plating with the desired thickness of nickel. On removal from the bath, the specimen was washed with distilled water and rapidly dried by evacuation in the diffraction camera and there examined before being finally microphotographed. In this way it was possible to be sure of the cleanliness and freedom from tarnish of both substrate and deposit surfaces. Except where otherwise stated, in order to avoid any possible disturbing effect upon the continuity of deposit, each nickel coating was built up to the desired thickness on a freshly prepared and examined copper substrate withoug interrupting the deposition process.

The Results.

The results of the first series of experiments are summarised in Table I. It will suffice to add that these results were independent of the range of deposit thicknesses, between 2000 and 30,000 A, examined and, further,

TABLE I.—THE EFFECT OF BATH COMPOSITION AND CURRENT DENSITY ON THE NORMAL TYPE OF CRYSTAL ORIENTATION IN NICKEL ELECTRODEPOSITED IN THE ABSENCE OF A SUBSTRATE INFLUENCE.

Bath (Temperature 45°).	Type of Orientation obtained with the Current Density (A/dcm.^{2})		
	0·3.	0·6.	1·2.
Weak . .	Strong (100)	Moderate (100)	Moderate or weak (100)
Strong . .	Strong (110)	Moderate (110), weak (100)	Strong (100)

that the nickel crystals were sub-microscopic in that they were not resolved at a 950 × magnification.

Similar deposition conditions were employed in the second series of experiments in which nickel was plated on macrocrystalline copper substrates. Deposits of 1000, 2000, 5000, 10,000, 20,000 and 30,000 A in thickness were prepared in most cases, and their surfaces examined by electron diffraction and finally microphotographed, though in some a less extensive range sufficed for our purpose. The results of these experiments need not be set forth in detail; it would be impossible to present them more clearly than by the representative microphotographs, Figs. 1, 2 and 3, and the corresponding diffraction patterns, Figs. 4, 5 and 6. These bring to light the surprising fact that, whilst the microphotographs preserve throughout their essential features, irrespective of the deposit depth, the corresponding diffraction patterns undergo a radical change in character with increasing thickness of the nickel deposit. Thus, apart from colour and the circular pitmarks which appeared on all the microphotographs of nickel coatings from 2000 A upwards, there was nothing to distinguish microphotographs of the macro-crystalline copper substrates from those of the deposits, no matter what their thickness. On the other hand, although these same nickel deposits up to 2000 A generally yielded spot patterns of dimensions characteristic of the normal nickel lattice constants, but otherwise similar in type to, and indeed hardly distinguishable from, Fig. 4, further increase in deposit thickness led to a gradual weakening of the diffraction spots and their replacement by rings and, finally, by arcs characteristic of submicroscopic crystals in an orientation typical of the deposition conditions in the absence of a specific substrate influence. The deposit depths at which the states represented by Figs. 5 and 6 were attained varied between about 2000 and 20,000 A, and between 10,000 and 30,000 A respectively, according to the deposition conditions. In general, the more favourable these conditions were to a strongly pronounced orientation, the more rapid was the loss of substrate influence, as reflected in the diffraction patterns, with increasing thickness of deposit.

In the course of further experiments in this series it was found that sometimes a mere interruption of the plating current or, with greater certainty, removal of the partly plated specimen from the bath followed by washing and examination in the camera effectively destroyed the substrate influence of the surface on any subsequently deposited nickel. For example, a specimen yielding a microphotograph similar to Fig. 2, and a diffraction pattern intermediate between Figs. 4 and 5 in regard to the relative proportions of large and small crystals indicated, was returned to the plating bath and a further layer of 5000 A deposited under conditions (weak bath and 1·2 A/dcm.^{2}) which should have led to a pattern similar to Fig. 5. The resulting pattern, however, exhibited no signs of large crystals but was typical of submicroscopic crystals in rather weak (100) orientation. On the other hand, the corresponding microphotograph again afforded no indication of the change in surface conditions, being essentially similar in type to Figs. 2 and 3. It is significant that, in the several cases encountered of such suppression of substrate influence, the upper nickel layer stripped readily from the lower which in its turn, however, adhered firmly to the copper substrate. This observation agrees with those previously made [2] according to which ability to follow, at least in its initial layers, the substrate crystal size and orientation is a *sine qua non* of good powers of adhesion in the deposit.

In regard to the results in the third series of experiments, it will suffice for the present purpose to record that the results agreed in general with those set forth above, except for the weaker substrate influence of the macrocrystalline cuprous oxide as compared with copper surfaces of similar crystal size; and this may have been due, at least in part, to the surface reduction to copper which occurred during the initial stages of deposition. Thus, here again, the microscope gave no indication of the profound changes occurring with increasing nickel deposit thickness in crystal size and orientation, and to which the electron diffraction patterns once more bore eloquent testimony.

Conclusions.

The revealing by the microscope of a faithful columnar preservation of the boundaries of the substrate copper macrocrystals throughout the nickel deposits would, in the absence of evidence to the contrary, normally suggest a like preservation of both crystal size and orientation. Others who have seen the microphotographs support us in this view. Electron diffraction, however, reveals a radical change in crystal size and orientation with increasing deposit thickness. Thus the outstanding fact disclosed by these experiments is that the microscope not only fails to give any indication of this, but even falsely suggests an absence of any such change, by the retention throughout the deposit of a network pattern of markings which begin with being real crystal outlines but which, unlike the similar networks in the cuprous oxide substrates, degenerate sooner or later into psuedo-single-crystal boundaries enclosing not one large, but many small crystals in a wholly different orientation to that of the original crystal. Apart from colour, the circular pitmarks are the one feature clearly differentiating the copper substrate microphotographs from those of the nickel deposit. But these must be independent of, and can therefore afford no indication of crystalline changes since, as has been pointed out above, such pitmarks appear before any change in crystalline structure can be detected by electron diffraction. They are probably due to hydrogen evolved during deposition.

Finch and Sun,[2] using sub-microscopic or microcrystalline massive substrates, noted a complete loss of substrate orientating effect at deposit depths within 2,000 A ; on the other hand, in the present experiments, the substrate influence on crystal size, and presumably therefore also on orientation, could still be detected under favourable circumstances at depths exceeding as much as 20,000 A. In this case, however, the substrates were macrocrystalline. Thus it may be inferred that the larger the substrate crystal size, the greater will be the deposit thickness throughout which the substrate influence on crystal size and orientation will make itself felt. It is reasonable to suppose that the gradual loss of such substrate characteristics in the deposit is due to a preferential deposition in the neighbourhood of those crystals which exert a substrate influence such as to lead to a crystal size and orientation similar to that favoured by the particular conditions of deposition. A macrocrystalline substrate is likely to present far fewer such growth centres than one of microcrystalline structure. Indeed, in the case of an undamaged single crystal substrate surface there seems to be no reason why under suitable conditions the substrate orientation, once adopted by the first few atomic layers, should ever be departed from, no matter how thick the deposit, provided the surface sustains no injury or disturbance during growth.

The diffraction patterns obtained in the course of these experiments so far afford no decisive evidence of a psuedomorphic or other type of lattice distortion imposed by the substrate on the deposit crystals. As can be plainly seen from Fig. 4, the extended spot heads remote from the shadow edge of the patterns have as *loci* the normal diffraction circles. The corresponding measurements of the diffraction patterns lead in all cases to the normal values for the lattice dimensions of copper, cuprous oxide and nickel. The cause of the extension of the spots into streaks will be discussed elsewhere on completion of experiments which are now in hand. This, however, is clear; the extension cannot be ascribed to poor resolution due to a small height of crystal elastically accessible to the electron beam because, if this were so, the streaks should be approximately bisected by the corresponding normal rings. Nor can we reasonably look to a refractive effect for the explanation because in some cases the extension is such as would lead to an inner potential exceeding 200 volts, a highly improbable value.

Summary.

The influence of macrocrystalline copper and cuprous oxide substrates on crystal size and orientation in nickel electrodeposits has been studied by micrographic and electron diffraction methods.

It has been found by electron diffraction that crystal size and orientation gradually depart from that exhibited by the substrate until, at deposit depths not exceeding 30,000 A, and generally much less under the conditions of our experiments, the nickel coating surface has a crystal size and orientation characteristic of the deposition conditions, but quite different from those of the substrate. Owing to the fact that the deposit reproduces faithfully and throughout its depth the network of crystal boundaries of the substrate, the microphotographs, which do not reveal the new submicroscopic crystal boundaries, falsely suggest a persistence of the substrate influence on, and continuity of, crystal size and orientation throughout the deposit.

It is considered that conclusions based on microscopic methods as to the retention of the crystal size and orientation of the basis metal by nickel and possibly also by other electro-deposits should be treated with reserve, unless confirmed by electron diffraction.

The main factors found to determine the crystal size of electro-deposited nickel are substrate influence and deposition conditions such as bath composition and current density. Large substrate crystal size coupled with deposition conditions leading to weakly pronounced or dual types of orientation favour the retention of substrate crystal size and orientation by the deposit, though with increasing thickness the influence of the deposition conditions becomes more pronounced and finally prevails.

Interrupting the deposition process sometimes leads to an abrupt suppression of the substrate influence in subsequently deposited nickel layers and reduction of adhesion.

We wish to thank the Westinghouse Brake and Signal Company Ltd. and Ferranti Ltd., for grants and apparatus.

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THE CATALYSIS OF THE MALEIC TO FUMARIC ACID ISOMERISATION BY HYDROGEN IONS.

By Charles Horrex.

Communicated by Professor Polanyi.

Received 10*th February*, 1937.

There has been considerable speculation concerning the mechanism by which the absence of rotation imposed by the double bond is overcome in the catalysed conversion of maleic to fumaric acid. If the acid catalysed isomerisation proceeds via the addition of H^+ (or HX) to the double bond :—

$$CO_2H.CH = CH.CO_2H \rightleftharpoons CO_2H.CH_2.\overset{+}{C}H.CO_2H$$

it can easily be seen from a spatial model that the added hydrogen atom will not be the one eliminated from the intermediate complex. The experimental results of the present communication show that in the isomerisation catalysed by aqueous hydrochloric acid containing high concentrations of deuterium there is no introduction of deuterium into the — CH = CH — system. This indicates that the geometrical inversion does not proceed by the above mechanism. Possible alternative views are that hydrogen ions can facilitate the reaction by combination with groups attached to the double bond,[1] or by the ionic field producing distortion and extension of the double bond in a manner similar to that suggested for certain paramagnetic catalysts.[2]

On dissolving either of the acids in heavy water it is to be expected that an equilibrium will be set up very rapidly between the ionised carboxyl hydrogen atoms and the deuterium in the solvent. The fumaric acid from inversion experiments with heavy aqueous acid would, therefore, contain deuterium atoms in the carboxyl groups but these atoms should be replaced by normal hydrogen if the acid is recrystallised from a large excess of normal water.

To ensure that only two of the four hydrogen atoms in the acid molecule can undergo exchange in this manner a preliminary experiment was made. 0·13 g. fumaric acid was heated to 100° in 2 c.c. 99·5 per cent. D_2O for fifteen minutes. The solid separated on cooling was combusted and the deuterium content of the water formed determined by density determinations with the micropyknometer.[3] Two separate combustions yielded water containing 47·6 and 49·0 per cent. D_2O respectively. Since the solvent D_2O was in large excess the replaceable hydrogen atoms would be almost completely exchanged. From the result obtained these replaceable hydrogen atoms are, as was expected, a half of the total number. A similar experiment with 65 per cent. D_2O gave a deuterium content of 33·3 per cent. in the fumaric acid. From the method of introduction the deuterium in the carboxyl groups can obviously be removed by recrystallisation from excess normal water.

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[1] Terry and Eichelberger, *J.A.C.S.*, 1925, *47*, 1402.

[2] R. Kuhn in Freudenberg's *Stereochemie*, 1933, p. 913.

[3] Gilfillan and Polanyi, *Z. physikal. Chem.*, *A*, 1933, *166*, 254.

The *cis-trans* conversion was carried out by heating 2 gm. of maleic acid in 1 c.c. 99·5 per cent. D_2O (2*N* in DCl) at 100° for an hour. The precipitated fumaric acid was recrystallised twice from a large excess of water, dried and combusted. The combustion water contained no deuterium. This experiment has been repeated with 1 c.c. 50 per cent. D_2O (2*N* in HCl) and 1½ c.c. 30 per cent. D_2O (3*N* in HCl), and analysis of the combustion waters for deuterium gave 0·04 per cent. and 0·01 per cent. of the heavy isotope. These figures are within the probable error of the experiments (0·05 per cent.) and are certainly very much less than would be expected under conditions where the conversion was proceeding by addition of the catalyst to the — CH = CH — system.

The maleic acid used in this work was obtained from Messrs. Hopkin and Williams, and recrystallised to m.p. 130·5° C. The fumaric acid used was prepared from it and recrystallised. Deuterium oxide (99·5 per cent.) was obtained from Messrs. Imperial Chemical Industries Ltd. and other concentrations prepared by dilution. Before use the water was twice distilled in vacuum. DCl was prepared from 98 per cent. D_2SO_4 (Messrs. I.C.I. Ltd.) and "A.R." NaCl; HCl was prepared in a similar manner and purified by vacuum distillations, the purified gases being dissolved in the purified heavy water to provide acid of the required normality. The combustions of the fumaric acid were carried out in a modification of the normal microanalysis furnace arranged to work under high vacuum. This has been shown to give satisfactory results from experience in this Department. The combustion waters were purified by two distillations in high vacuum.

I wish to thank Professor M. Polanyi for suggesting this work and Mr. G. N. Copley and Mr. R. K. Greenhalgh for experimental assistance.

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Manchester.

KINETIC-RADIOACTIVE INVESTIGATIONS ON THE ACTIVE SURFACE OF CRYSTALLINE POWDERS.

By L. Imre.

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According to the modern theory of crystal growth, as developed by Volmer, Kossel, Stranski and co-workers,[1] any changes in the surface area or in mass of crystals in contact, *e.g.*, with their solutions, follow one or both of the following two processes: (1) Formation of two-dimensional nuclei, in consequence of the condensation of atoms on already existing lattice planes, or of the partial dissolution of complete lattice planes. (2) Addition of two-dimensional nuclei to complete lattice planes by successive adherence (adsorption) of individual atoms on the boundary of the two-dimensional nuclei, or, on the other hand, disappearance of such nuclei due to the successive dissolution of their boundary constituent atoms.

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* One part of the original having been published in *Z. Physik. Chem.*, 8th September, 1936.

[1] (*a*) M. Volmer and A. Weber, *Z. physik Chem.*, 1926, **119**, 277. (*b*) M Volmer and M. Marder, *ibid.*, 1931, **154**, 97. (*c*) M. Volmer and W. Schultze, *ibid.*, *A*, 1931, **156**, 1. (*d*) W. Kossel, *Leipziger Vorträge*, 1928, 1. (*e*) I. N. Stranski, *Z. physik. Chem.*, 1928, **136**, 259. (*f*) I. N. Stranski and R. Kaischew, *Physik. Z.*, 1935, **36**, 402. (*g*) I. N. Stranski and R. Kaischew, *Ann. Physik.* (5), 1935, **23**, 330.

Now, according to theory, the first processes occur only when the surrounding solution is supersaturated (or undersaturated) with respect to the crystal. In the case of an exactly saturated solution the individual atoms (or ions) which strike a *complete* lattice plane surface stay there as adsorbed single atoms only for a very short time, unless neighbouring atoms are adsorbed (*i.e.*, for a short time relatively to the number of all the atoms striking the surface); the probability of formation of a new stable surface element, with many atoms connected with one another, is therefore zero. Experience has fully verified this conclusion.[1(c)]

The second process seems, however, to occur also in the absence of oversaturation (or undersaturation). For instance,[2] highly dispersed precipitates, colloids, freshly prepared powders of microscopic crystals, etc., frequently change their structure when shaken for a time with their saturated solutions. By such "aging," the powder grains become larger and larger with time and, moreover, their lattice structure sometimes becomes more regular; this must be due to *active spots* of the surface, on which the imperfect surface elements of the crystal can grow (or go in solution), owing to the adsorption (or desorption) of individual atoms.

The elementary processes so far observed in the equilibrium of heterogeneous systems consisting of crystals and their saturated solutions, seem to accord fully with this scheme. The most characteristic, the immediate exchange of atoms between solution and solid (the upper atomic layer of the crystal), has been studied systematically by Paneth [3] with the aid of radioactive isotopes. When one shakes, *e.g.*, lead sulphate powder with its saturated solution, in which radioactive $Pb^{\cdot\cdot}$ ions (*e.g.*, ThB) are dissolved, a continuous kinetic exchange takes place between the dissolved $Pb^{\cdot\cdot}$ (ThB) ions and the Pb atoms of the upper surface layer of the solid, whereby part of the ThB passes over to the solid wall. With well "aged," relatively large and regular crystals there is soon a definite partition state between the precipitated and the dissolved ThB ions, corresponding to the ratio of the numbers of $Pb^{\cdot\cdot}$ ions in the solid wall and solution respectively. Clearly there is practically no other process taking place, except the exchange process on the surface of relatively regular crystals; in particular, there is no Langmuir adsorption.

If, however, the crystal powder has been prepared by sudden precipitation and insufficiently "aged" no sharply defined partition equilibrium of the radioactive ion can be attained experimentally by Paneth's method; the exchange values increase with time, even after several hours of shaking.[4] According to the author, these prolonged surface phenomena are closely related to the coarsening of the fine salt powder, the *recrystallisation* of which builds up further imperfect surface lattice planes on active spots by adsorption of dissolved ions. and simultaneous solution of other active surface elements. In this way the ThB atoms taken up by the solid wall by a Paneth exchange process are gradually incorporated in deeper and deeper layers of the crystal lattice, as if they were diffusing there very rapidly. This analogy is, of course, very superficial; it might perhaps be called "pseudo-diffusion"; real diffusion in solids is an extremely slow process,[5] which cannot account for the phenomena treated here. Recently Kolthoff and his collaborators [6] developed a somewhat similar idea of the recrystallisation effects, in their systematic studies on structural changes of freshly formed precipitates.

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[2] H. Freundlich and E. Haase, *Z. physik. Chem.*, 1915, **89**, 417. I. M. Kolthoff and Ch. Rosenblum, *J. Amer. Chem. Soc.*, 1933, **55**, 2656. E. J. Verwey and H. R. Kruyt, *Z. physik. Chem.*, *A*, 1933, **167**, 137. L. Imre, *ibid.*, 1930, **146**, 41, etc.

[3] F. Paneth, *Z. Elektrochem.*, 1922, **28**, 113.

[4] L. Imre, *Z. physik. Chem.*, *A*, 1930, **146**, 41; 1931, **153**, 127, 262; 1933, **164**, 327; *Z. angew. Chem.*, 1930, **43**, 875; *Z. El.*, 1932, **38**, 535.

The author [7] has recently treated the mechanism of the above-pictured prolonged incorporation of ions in the crystal lattice by recrystallisation effects, in a more exact, quantitative manner for the special case when the rate of incorporation is relatively small; very simple relations between the rate of incorporation and the number of active spots on the surface can be derived. While the *static* partition equilibrium of the radioactive isotopes of the ions, according to Paneth, indicates the absolute magnitude of the surface layers in which the exchange takes place, the *kinetic* changes of the partition state are, in the author's opinion, characteristic of the active portion of the surface, *i.e.*, of that part on which a Langmuir adsorption of the ions can take place.

We here discuss some newer experiments with special regard to the practical possibility of the determination of the number of the active spots on the surface by the aid of radioactive methods, measuring the incorporation velocity of a radioactive isotope of the crystal-constituent ions in the lattice. The investigations are confined to relatively small velocities; a more general method and theory will be discussed later.

Experimental.

The lead isotope ThB was the most convenient radioactive body; the different lead salts had to be capable not only of effecting an easily measurable exchange with dissolved ThB-ions, but also of absorbing lead ions (*e.g.* as lead nitrate) in appreciable quantities. This was necessary, when one had to derive the active spots of the surface both directly from the adsorption isotherm and indirectly from the incorporation velocity of ThB in the crystal. The experimental proof of the theory involved comparison of the two sets of values found.

Radioactive measurements can be made in many ways but a sufficiently accurate direct proof of adsorption was possible only with a few, slightly soluble, lead salts, and even this only when these salts had been specially prepared in order to make the surface as large as possible.

Lead iodide was prepared from $Pb(NO_3)_2$ (Kahlbaum), recrystallised four times from hot water, containing some HNO_3, and from KI "pro analysi" Merck. The solutions (0·4 *M* $Pb(NO_3)_2$ and 0·8 *M* KI) were mixed, litre by litre, at 0° C. with rapid stirring. In all, about 2000 gm. were collected, purified, and "aged" by washing daily for about two months with 3-4 litres of distilled water of 0° C., then dried and afterwards kept in an exsiccator over granulated $CaCl_2$.

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[5] *Cf.* G. Hevesy and W. Seith, *Z. physik.*, 1929, **56**, 790.

[6] I. M. Kolthoff, W. v. Fischer and Ch. Rosenblum, *J. Amer. Chem. Soc.*, 1934, **56**, 382.

[7] L. Imre, *Z. physik. Chem.*, *A*, 1936, **177**, 409.

Lead sulphate, prep. (A) was made similarly by mixing 0·2 M lead acetate " pro analysi " Merck (containing some HNO_3 to retard hydrolysis) and 0·2 M sulphuric acid " pro analysi " Merck, at 20° C. The preparation was washed once with hot distilled water, then with distilled water at room temperature for about two months.

Lead sulphate, prep. (B) was made by mixing solid lead acetate powder (" pro analysi " Merck) with the equivalent quantity of concentrated H_2SO_4 (" pro analysi " Merck). The preparation was washed with distilled water at room temperature for about one month, then four times with hot distilled water, then again with distilled water at room temperature for about one month.

Lead chromate was prepared from hot 0·1 M $Pb(NO_3)_2$ (Kahlbaum), four times recrystallised, and 0·1 M solutions K_2Cro_4 " pro analysi " Merck. The preparation (about 1500 gm.) was washed daily with about 4-5 litres of hot distilled water for about 6 months, then dried, etc.

The microscopically measured dimensions of the particles were .

PbI_2 : average length = $12\cdot50 \times 10^{-4}$ cm.
average width = $10\cdot20 \times 10^{-4}$ cm.
specific surface = $8\cdot96 \times 10^{2}$ cm.^{2} (specific weight = 6·16).
The surface of 1 gm. contains : $X = 5\cdot96 \times 10^{-2}$ gm. moles PbI_2.

$PbSO_4$, A : average length = $10\cdot12 \times 10^{-4}$ cm.
average width = $6\cdot16 \times 10^{-4}$ cm.
specific surface = $1\cdot20 \times 10^{3}$ cm.^{2} (specific weight = 6·23).
The surface of 1 gm. contains : $X = 1\cdot06 \times 10^{-6}$ gm. moles $PbSO_4$.

$PbSO_4$, B : average length = $5\cdot04 \times 10^{-4}$ cm.
average width = $3\cdot40 \times 10^{-4}$ cm.
specific surface = $2\cdot70 \times 10^{3}$ cm.^{2} (specific weight = 6·23).
The surface of 1 gm. contains : $X = 2\cdot39 \times 10^{-6}$ gm. moles $PbSO_4$.

$PbCrO_4$: average length = $34\cdot06 \times 10^{-4}$ cm.
average width = $3\cdot08 \times 10^{-4}$ cm.
specific surface = $2\cdot32 \times 10^{3}$ cm.^{2} (specific weight = 6·123).
The surface of 1 gm. contains : $X = 1\cdot95 \times 10^{-6}$ gm. moles $PbCrO_4$.

The numbers of the gram moles contained in the surface of 1 gm. substance were computed by dividing the specific surface by the product of the Avogadro number (= $6\cdot06 \times 10^{23}$) by the elementary surface, this latter (= Δf) having been derived from the molecular weight (M) of the substance of the crystal, the specific weight (= σ) and the Avogadro number :

$$\Delta f = \left(\frac{M}{6\cdot06 \times 10^{23} \times \sigma}\right)^{\frac{2}{3}}.$$

1. Adsorption Measurements.

The object of these was a direct determination of the number (z) of active spots on the surface, on the basis of Langmuir's isotherm equation :

$$c/a = 1/z \,.\, c + b \qquad . \quad . \quad . \quad . \quad (1)$$

where c = concentration of the adsorbed substance in the adsorption equilibrium, a = adsorbed quantity, b = constant (for a given system and temperature).

Lead Iodide.—Samples of 50 gm. PbI_2 were stirred for half an hour each with lead nitrate solutions, already saturated with PbI_2, at 0° C. (velocity of the stirring : 450-480 turns per minute with a simple glass propeller), then filtered quickly through membrane filters (" 6 second "), which had already been cooled to 0° C. The filtrates were then warmed to room temperature and 20 c.c. were analysed by the known lead chromate method, titrating the lead iodometrically by 0·01 *N* $Na_2S_2O_3$. The results are collected in the Table I.

It is seen that no adsorption could be detected with certainty; having regard to the apparently limited accuracy of the method, one can only say that there was no adsorption greater than about 1 per cent.

In the two other adsorption systems,

$PbSO_4 - P(NO_3)_2$

and

$PbCrO_4 - Pb(NO_3)_2$

the Pb·· ion concentrations to be determined were too slight for the iodometric method and a colorimetric method was necessary. The *photo-cell colorimeter* by B. Lange[8] was found to be entirely satisfactory. Actually the modified photoelectric instrument of P. Roth,[9] was used.[10]

This instrument was used as follows: The Pb·· ion solutions to be examined were under regulated stirring, poured into

TABLE I.—THE ADSORPTION OF LEAD NITRATE BY LEAD IODIDE AT 0° C

Adsorbent: 50 *gm.* PbI_2 *with* 50 *c.c* solution.

Concentration of $Pb(NO_3)_2$ in the Starting Soln in gm. moles/litre × 10^{-3}.	Total Concentration of Pb·· in the Saturated Solution, gm. moles/litre—		Concentration of $Pb(NO_3)_2$ after the Ads Exp., in gm. moles/litre × 10^{-3}.	Adsorption, Per cent.
	Before the Ads. Exp × 10^{-3}.	After the Ads. Exp. × 10^{-3}.		
1	1·654	1·649	0·995	+0·5
1	1·655	1·652	0·997	+0·3
1	1·660	1·670	1·010	−1·0
1	1·675	1·668	0·993	+0·7
2	2·564	2·548	1·982	+1·0
2	2·520	2·543	2·023	−1·2
2	2·417	2·420	2·003	−0·2
2	2·545	2·540	1·995	+0·3
3	3·478	3·475	2·997	+0·1
3	3·480	3·480	3·000	0·0
3	3·450	3·440	2·990	+0·3
3	3·420	3·430	3·010	−0·3

TABLE II.—THE ADSORPTION OF LEAD NITRATE BY LEAD SULPHATE.

Adsorbent: 60 *gm.* $PbSO_4$, prep. *A.*, *with* 50 *c.c.*^{3} *solution.*

Concentration of $Pb(NO_3)_2$ in the Starting Solution, gm moles/litre. × 10^{-4}	Total Concentration of Pb·· in the Saturated Solution, gm. moles/litre—		Concentration of $Pb(NO_3)_2$ after Adsorption, gm moles/litre. × 10^{-4}.	Adsorption Per Cent.
	Before Adsorption. × 10^{-4}.	After Adsorption × 10^{-4}.		
(a) At 0° C.				
1·65	2·26	2·26	1·65	0·0
1·65	2·27	2·26	1·64	+0·7
3·00	3·38	3·38	3·00	0·0
3·00	3·38	3·39	3·01	−0·3
5·00	5·26	5·23	4·97	+0·6
5·00	5·24	5·25	5·01	−0·2
(b) At 20° C.				
1·65	2·47	2·48	1·66	−0·7
1·65	2·48	2·47	1·65	+0·6
3·00	3·58	3·55	2·97	+1·0
3·00	3·58	3·58	3·00	0·0
5·00	5·37	5·37	5·00	0·0
5·00	5·35	5·34	4·99	+0·4

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[8] M. Bendig and H. Hirschmüller, *Z. anal. Chem.*, **92**, 1, 933.

[9] Hungarian Patent No. 113,286.

[10] The author is indebted to the firm Erdély and Szabó, Budapest, for lending a Lange-Roth photocell colorimeter for the present investigations.

sufficient 0·1 $M Na_2S$, the time of this operation was noted and taken as the zero time. The light absorption caused by the coloured suspension was then measured over several minutes and the time-absorption curve so obtained was graphically extrapolated to zero time. The extrapolated values were then taken as the basis for the determination of the corresponding concentrations, with calibrating curves constructed empirically with standard $Pb(NO_3)_2$ solutions of known concentration, treated in precisely the same way as the unknown solutions. This procedure seemed necessary, especially because of the gradually, though mostly very slow, coarsening of the suspensions, during which also their light absorption power increased with time; a reliable basis for accurate measurements was available only when taking into account this coarsening. The measurements were reproducible within an average error of some 1·5 to 2 per cent., in favourable cases the uncertainty being even less.

Tables II. to IV. contain the data. With the $PbSO_4$, prep. A., no adsorption could be detected with certainty, but possibly an adsorption

TABLE III.—THE ADSORPTION OF LEAD NITRATE BY LEAD SULPHATE.

Adsorbent: 60 *gm.* $PbSO_4$, *prep B, with* 30 *c.c. solution*
Temperature: 20° C.

Concentration of $Pb(NO_3)_2$ in the Starting Solution, in gm moles/litre. × 10^{-4}.	Total Concentration of $Pb^{\cdot\cdot}$ in the Saturated Solution, in gm moles/litre— Before Adsorption × 10^{-4}.	After Adsorption × 10^{-4}	Concentration of $Pb(NO_3)_2$ after Adsorption, in gm moles/litre (c). × 10^{-4}.	Adsorption Per Cent	
1	2·030	2·005	0·975	+2·5	average +2·0 per cent
1	2·028	2·020	0·992	+0·8	
1	2·030	2·014	0·984	+1·6	
1	2·035	2·005	0·870	+3·0	
2	2·780	2·748	1·968	+1·6	average: +0·8 per cent.
2	2·778	2·768	1·990	+0·5	
2	2·780	2·762	1·982	+0·0	
2	2·770	2·774	1·998	+0·1	
3	3·587	3·590	3·003	-0·1	average. +0·6 per cent.
3	3·592	3·530	2·958	+1·4	
3	3·596	3·582	2·986	+0·5	
3	3·590	3·568	2·978	+0·6	

$z \sim$ about 1·5 × 10^{-7} gm. moles per 60 gm. $PbSO_4$.
$z \sim$ about 2·10 × 10^{-9} gm. moles per 1 gm. $PbSO_4$.
The "active portion" of the surface: $z/X \sim$ ca. 1·5 × 10^{-4}.

less than 1 per cent. actually took place. In the case of the $PbSO_4$, prep. B., the direct concentration measurements indicated an adsorption, but even with this preparation, which had a very large specific surface, the adsorption values were not essentially greater than the uncertainty of the method. Thus, the number of the active spots (z) and the "active fraction" of the surface, *i.e.*, the ratio of the number of the active spots to the total number of the Pb atoms of the surface, could only be estimated in the order of magnitude.

From the data on the system $PbCrO_4 - Pb(NO_3)_2$, two different values of (z) could be derived from, respectively, the lower concentrations (above the dotted line in Table IV.), and the larger concentrations (under the dotted line) (see Table IV). There seem to be possibly some very active spots on the surface and at the lower Pb•• concentrations adsorption takes place only on these, when they are gradually occupied, the other, less active, but more numerous, spots come into play. Now, since the radioactive measurements to be described later were carried out in the absence of lead nitrate, the values of z and z/X for small Pb•• concentrations will be more comparable with the results of the radioactive measurements than those for large concentrations.

TABLE IV.—EXPERIMENTS ON THE ADSORPTION OF LEAD NITRATE BY LEAD CHROMATE.

Adsorbent : 5 *gm.* $PbCrO_4$ in 50 *cm* ^{3} *solution.*

Concentration of $Pb(NO_3)_2$, gm. moles/litre —		Adsorption Per Cent.
Before Adsorption. $\times 10^{-5}$.	After Adsorption $\times 10^{-5}$	
(a) At 0° C.		
1·0	0·180	82·0
1·5	0·480	68·0
2·0	0·670	66·5
2·5	1·200	52·0
3·5	1·800	48·5
5·0	3·080	38·4
7·0	4·750	32·1
10·0	7·65	23·5
(b) At 20° C.		
1·0	0·270	73·0
1·5	0·600	60·0
2·0	1·125	48·8
2·5	1·375	45·1
3·5	2·200	37·2
5·0	3·500	30·0
7·0	5·10	27·2
10·0	7·92	20·8

$$\left.\begin{aligned} z &= 1{\cdot}3 \times 10^{-7} \text{ gm. moles per gm. } PbCrO_4 \\ z/X &= 6{\cdot}67 \times 10^{-2} \text{ gm. moles per gm. } PbCrO_4 \end{aligned}\right\}$$

for small Pb•• concentrations.

$$\left.\begin{aligned} z &= 2{\cdot}74 \times 10^{-7} \text{ gm. moles per gm. } PbCrO_4 \\ z/X &= 1{\cdot}41 \times 10^{-1} \text{ gm. moles per gm. } PbCrO_4 \end{aligned}\right\}$$

for large Pb•• concentrations.

2. Radioactive Measurements on the Incorporation Velocity of Pb•• Ions in the Surface Layers of Lead Salts in Contact with their Saturated Aqueous Solutions.

The general course of work with the radioactive atomic species ThB, used here, has been described previously by the author. It suffices to say that the crystal powder samples were stirred with the respective solutions at the temperatures in question for about thirty minutes each *before* the actual experiment, partly with the object of attaining a good temperature, and solution, equilibrium throughout the system, and partly in order to destroy lumps of crystal particles present in the dried preparation and, thus, to wet the whole surface. Only then were the systems mixed with ThB and the actual experiment begun.

The solutions of the ThB were weakly acid (2×10^{-3} $N . HNO_3$), in order to prevent formation of "radiocolloids."[11] The velocity of stirring was between 450 and 480 turns per minute.

The results are collected in the Table V. The values of incorporated ThB, calculated from the simple equation[12]

$$x = -A_1 . e^{-a_1 t} - A_2 . e^{-a_2 t} + A_3 \quad . \quad . \quad . \quad (2)$$

are shown as "$x_{\text{calc.}}$". (In general: x = the fraction of ThB which has already passed over from the solution into the crystal during time t, *all* the ThB having been originally in the solution at the beginning of each experiment.)

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[11] O. Hahn and L. Imre, *Z. physik. Chem.*, 1929, **144**, 173.

[12] L. Imre, *ibid.*, *A*, 1931, **153**, 262.

TABLE V.—Incorporation of ThB in the Surface Layers of Lead Salts.

Time in Hours.	$x_{\text{exp.}}$	$x_{\text{calc.}}$	Time in Hours.	$x_{\text{exp.}}$	$x_{\text{calc.}}$	Time in Hours.	$x_{\text{exp.}}$	$x_{\text{calc.}}$
1. Lead Iodide. (Suspension: 6 gm. PbI_2 in 50 c.c. sol. Temp.: 0° C. Conc. of HNO_3: $1{\cdot}5 \times 10^{-3}$ *N*. Solubility of PbI_2 $0{\cdot}953 \times 10^{-6}$ gm. moles/c.c.)								
0·05	0·151	0·171	0·45	0·227	0·231	3·00	0·352	0·3515
0·10	0·170	0·180	0·50	0·248	0·237	4·20	0·361	—
0·15	0·197	0·188	0·60	0·255	0·248	5·00	0·364	—
0·20	0·188	0·196	0·80	0·276	0·268			
0·25	0·212	0·204	1·00	0·282	0·284	$x_\infty = 0{\cdot}364$		
0·30	0·217	0·211	1·40	0·316	0·290	$x_{\text{calc.}} = -0{\cdot}202 \times e^{0{\cdot}903t} + 0{\cdot}364$		
0·35	0·210	0·218	2·00	0·332	0·332			
2. Lead Sulphate.—(Suspension: 3 gm. $PbSO_4$, prep. A., in 50 c.c. sol. Temp.: 20° C. Conc. HNO_3 $1{\cdot}5 \times 10^{-3}$ *N*. Solubility of $PbSO_4$ = $1{\cdot}45 \times 10^{-7}$ gm. moles/c.c.)								
0·05	0·278	0·275	0·45	0·398	0·417	2·00	0·552	0·554
0·10	0·301	0·299	0·50	0·430	0·420	3·20	0·556	0·563
0·15	0·322	0·320	0·65	0·472	0·459	5·00	0·564	—
0·20	0·332	0·340	0·80	0·479	0·483	7·00	0·565	—
0·30	0·388	0·375	1·10	0·502	0·516	$x_\infty = 0{\cdot}565$		
0·40	0·386	0·404	1·40	0·513	0·546	$x_{\text{calc.}} = -0{\cdot}315 \times e^{1{\cdot}683t} + 0{\cdot}565$		
3. Lead Sulphate.—(Suspension: 1·5 gm. $PbSO_4$, prep. B., in 50 c.c. sol. Temp.: 20° C. Conc. HNO_3 = 10^{-1} *N*. Solubility of $PbSO_4$ = $1{\cdot}45 \times 10^{-7}$ gm. moles/c.c.)								
0·05	0·407	0·412	0·70	0·561	0·555	4·00	0·654	—
0·10	0·428	0·424	0·95	0·583	0·587	5·20	0·660	—
0·15	0·456	0·433	1·20	0·632	0·608	6·50	0·658	—
0·25	0·461	0·466	1·60	0·610	0·620	$x_\infty = 0{\cdot}660$		
0·35	0·503	0·501	2·00	0·642	0·642	$x_{\text{calc.}} = -0{\cdot}265 \times e^{1{\cdot}364t} + 0{\cdot}660$		
0·50	0·526	0·525	2·80	0·646	0·652			
4. Lead Chromate.—(Suspension: 0·2 gm. $PbCrO_4$ in 50 c.c. sol. Temp.: 20° C. Conc. HNO_3: 10^{-4} *N*. Solubility of $PbCrO_4$ $1{\cdot}958 \times 10^{-9}$ gm. moles/c.c.)								
0·02	0·516	0·546	0·30	0·786	0·775	2·00	0·883	0·882
0·03	0·625	0·631	0·40	0·796	0·794	6·50	0·886	
0·05	0·692	0·689	0·50	0·812	0·810	10·00	0·887	
0·10	0·727	0·724	0·60	0·828	0·823			
0·15	0·747	0·739	0·80	0·843	0·842	$x_\infty = 0{\cdot}887$		
0·20	0·747	0·752	1·00	0·864	0·856	$x_{\text{calc.}} = -0{\cdot}695 \times e^{78{\cdot}74t} - 0{\cdot}185 \times e^{1{\cdot}846t} + 0{\cdot}887$		
0·25	0·772	0·764	1·40	0·870	0·872			
5. Lead Chromate.—(Suspension: 0·05 gm. $PbCrO_4$ in 50 c.c. sol. Temp.: 20° C. Conc. HNO_3 = 10^{-4} *N*. Solubility of $PbCrO_4$ = $1{\cdot}958 \times 10^{-9}$ gm. moles/c.c.)								
0·02	0·202	0·202	0·40	0·540	0·522	4·00	0·704	—
0·03	0·286	0·268	0·50	0·546	0·544	4·80	0·718	—
0·05	0·344	0·347	0·70	0·590	0·580	7·00	0·706	—
0·10	0·427	0·426	1·00	0·635	0·620			
0·15	0·444	0·443	1·50	0·662	0·662	$x_\infty = 0{\cdot}706$		
0·20	0·482	0·470	2·00	0·697	0·681	$x_{\text{calc.}} = -0{\cdot}415 \times e^{-34{\cdot}50t} - 0{\cdot}303 \times e^{-1{\cdot}251t} + 0{\cdot}706$		
0·25	0·490	0·484	2·40	0·706	0·692			
0·35	0·498	0·510	3·00	0·683	—			

It is seen that the phenomenon can be represented very well by such a simple equation, if there is no longer an appreciable velocity after the fourth to fifth hour, so that the state of the system can then be considered practically as an equilibrium with respect to the partition of ThB between the crystal mass and the liquid. With the lead salt preparations used this permits quite a good approximation, and equation (2) seems a correct basis for discussion of the experimental material.

Discussion and Summary.

All phenomena, in which the same number of atoms exchange their binding states, are, as a rule, considered in the literature as "exchange processes." To understand the proper mechanism of such processes, it seems, however, necessary first to distinguish and classify them according as to whether the exchange takes place in *one* elementary reaction by pairs of atoms, or in two, locally separated, elementary processes. In the first case one speaks of an immediate interchange of atoms, while in the second the conception of "exchange reaction" has only a statistical meaning.

In our case of heterogeneous systems this contrast of the two classes of exchange reactions is very conspicuous: the immediate interchange of atoms on the boundary surface, *i.e.* the exchange process studied by Paneth, proceeds without change of structure of the solid, while the separated processes of incorporation of single atoms in the crystal and of similtaneous dissolution of other single atoms from the crystal result necessarily in a structural change of the surface. It therefore seems necessary in the mathematical treatment, also to separate the Paneth exchange process from the "pseudo-diffusion" or incorporation process.

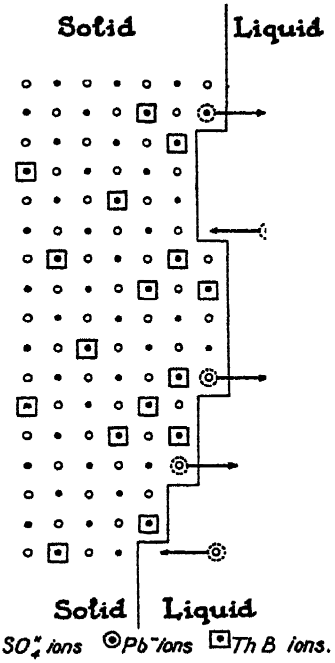

FIG. 1.

The kinetics of the Paneth process can be represented [13] by the following equation:

$$\frac{dx_1}{dt} = w_1 \cdot y - w_{-1} \cdot x_1 + w \cdot (x_2 - x_1) \quad . \quad . \quad (3)$$

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[13] L. Imre, *Z. physik. Chem.*, *A*, 1936, 177, 416, Eqn. (10). In this paper the quantity of ThB in the first atomic layer has been designated x_2, that in the second layer x_3, etc. This system of designation originates in previous investigations on colloidal silver haloids, when it was necessary to reserve the symbol x_1 for the atoms in the diffuse double layer. It seems, however, better to use for the latter some other symbol, and to designate by x_1 the first layer of the solid, etc.

where y, x_1, x_2, x_3 are the quantities of ThB respectively in the solution, and in the first, second and third atomic layers of the solid at time t; w_1 the velocity of passage of the dissolved ions into the surface, w_{-1} that of the ions of the solid wall into the solution, and w that of any atomic layer of the solid into the next atomic layer. The numerical values of these velocities can be expressed by the absolute magnitude of the surface, F, the diffusion constant of the dissolved molecules, D, the thickness of the solvent layer at the solid surface, δ (Nernst-Brunner), the volume of the solution, v, the solubility of the crystal, C, the quantity of substance in the surface layer, X, and the number of active spots of the surface, z, as follows:

$$w_1 = F \,.\, D/\delta \,.\, 1/v\,;\quad w_{-1} = C/X \,.\, F \,.\, D/\delta\,;\quad w = C \,.\, F \,.\, D/\delta \,.\, z/X^2. \qquad (4)$$

In order to represent the mechanism of the second type of exchange, *i.e.*, "pseudo-diffusion" or prolonged incorporation in the crystal due to recrystallisation effects, the following picture has been proposed (see Fig. 1): When the crystal grows, in consequence of a recrystallisation at some spots of its surface by an elementary fragment (precipitation, *e.g.*, of $Pb^{\cdot\cdot}$ or SO_4'' ions on the surface of $PbSO_4$), one atom of the (i)-th atomic layer of the solid passes over to the state of an atom of the ($i + 1$)-th layer of the newly-formed lattice. Thus, if in unit time n molecules of the crystal substance, originally dissolved, are precipitated, the same number of ions (n) of the (i)-th layer seem to have moved into the ($i + 1$)-th layer of the lattice. Now, if X be the total number of $Pb^{\cdot\cdot}$ ions in one layer, having the fraction x_i/X as radioactive (ThB) ions, then clearly $n \times x_i/X$ ThB ions of the (i)-th layer will in unit time pass over to the ($i + 1$)-th layer of the newly-formed lattice. In the same way, after dissolving m molecules on some spots of the surface (*e.g.*, the $Pb^{\cdot\cdot}$ or SO_4'' ions of the solid wall in Fig. 1 passing over to the liquid phase), $m \times x_i/X$ ThB ions, originally of the (i)-th layer, will now be in the ($i - 1$)-th layer of the newly-formed lattice. There is thus a continuous movement of an arbitrary ion inside the lattice, *relatively to the surface*, the latter being continuously pushed forwards and backwards by precipitation or dissolution of single ions of the crystal substance.

Now the number n and m can be expressed[13] as follows:

$$n = m = C \,.\, F \,.\, D/\delta \,.\, z/X = w \,.\, X$$

and so the incorporation of ThB in the crystal is represented by the following system of equations:

$$\left.\begin{aligned} \frac{dx_2}{dt} &= w \,.\, (x_1 - x_2) - w \,.\, (x_2 - x_3) \\ \frac{dx_3}{dt} &= w \,.\, (x_2 - x_3) - w \,.\, (x_3 - x_4) \end{aligned}\right\} \qquad (5)$$

etc.

If the surface of the crystal is very large, then in the first part of the phenomenon the Paneth exchange process, represented by eqn. 3, the *stationary* state is attained very rapidly. From eqn. 3 and 4 it can readily be computed that with such large surfaces as those of the samples of preparations referred to in the Table V. (1) to (3), the velocity of the Paneth exchange process must have been so very large that the stationary state is practically attained during a time much less than one minute, having then the relation:

$$x_1 = k \,.\, y, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where k is the time-independent partition coefficient between the surface and the solution. To a first approximation, *i.e.*, when w is small relative to w_1 and w_{-1}, it is: $k \gtrsim w_1/w_{-1} = X/vC$; this is the well-known relation of Paneth. Thus, in the case of relatively large surfaces (*e.g.* when $F \geqq$ about 500 cm.^{2} and $v \leqq$ about 50-100 c.c.), the equation system 5 has the form:

$$\left.\begin{aligned} \frac{dx_2}{dt} &= w \,.\, k \,.\, y - w \,.\, x_2 - w \,.\, (x_2 - x_3) \\ \frac{dx_3}{dt} &= w \,.\, (x_2 - x_3) - w \,.\, (x_3 - x_4) \end{aligned}\right\} \quad . \quad . \quad (5')$$

etc.

Another simplification can be made by taking into account the values of incorporated ThB when the process is already so slow that it can be looked upon practically as an equilibrium state. The data of Table V. show that, in the case of the lead salts in question, the final partition ratios, attained in some 4-5 hours (marked in the table as x_∞/y_∞) were never greater than about $3 \,.\, X/vC$, *i.e.*, the total quantities of incorporated ThB were not greater than those corresponding to about 3 atomic layers of the solid. Of course, this does not mean that *all* the ThB ions stay in one of the first three layers; on the contrary, it seems probable that some have gone deeper and, accordingly, in the partition state attained in some 4-5 hours, the density of ThB is not the same throughout the atomic layers concerned. But, since the layers, according to Fig. 1, do not differ from one another with respect to the probability of the process (which is represented by w for *all* atom layers of the solid) the whole process can, for the purpose of the mathematical treatment, be looked upon as if *only* the first three layers take part. Thus, we have the following system:

$$\left.\begin{aligned} \frac{dx_2}{dt} &= w \,.\, k \,.\, y - w \,.\, x_2 - w \,.\, (x_2 - x_3) \\ \frac{dx_3}{dt} &= w \,.\, (x_2 - x_3) - w \,.\, x_3, \end{aligned}\right\} \quad . \quad (6)$$

or, since $x_1 + x_2 + x_3 = x$, and $x_1 = k \,.\, y$, $\frac{dx_1}{dt} = k \,.\, \frac{dy}{dt}$,

$$\frac{dx}{dt} = \frac{dx_1}{dt} + \frac{dx_2}{dt} + \frac{dx_3}{dt} = k \,.\, \frac{dy}{dt} + w \,.\, k \,.\, y - w \,.\, (x_2 + x_3). \quad (7)$$

Expressing x_1, x_2, etc., as fractions of the total quantity of ThB, *i.e.*, taking $x_1 + x_2 + x_3 + y = 1$, we obtain: $y = (1 - x)$; $(x_2 + x_3) = x - x_1 = x - k \,.\, y = x - k \,.\, (1 - x) = (1 + k) \,.\, x - k$ and so, finally:

$$\frac{dx}{dt} = -\frac{1 + 2k}{1 + k} \,.\, w \,.\, x + 2w \,.\, k. \quad . \quad . \quad . \quad (8)$$

The solution of this equation is of the form:

$$x = -A_2 \,.\, e^{-a_2 t} + A_3 \quad . \quad . \quad . \quad (8')$$

where:

$$a_2 = \frac{1 + 2k}{1 + k} \,.\, w, \text{ that is } w = \frac{1 + k}{1 + 2k}. \quad . \quad . \quad (9)$$

At the beginning of the process represented by eqn. 8 one has only the partition of the ThB between the first surface layer and the solution (x_2 and x_3 being equal to zero at the beginning). It is therefore

$$k = \left(\frac{x}{y}\right)_{t\rightarrow 0} = \left(\frac{x}{1-x}\right)_{t\rightarrow 0} = \frac{-A_2+A_3}{1+A_2-A_3}. \quad . \quad (9')$$

In the two other systems (Table V. (4) to (5)) the surface of the crystal samples was not very large, so that the stationary partition state between x_1 and y was not attained so rapidly as in Table V. (1) to (3). The velocity of the Paneth exchange process could be measured here and represented by a further exponential function,[14] corresponding to eqn. 3, giving the more general relation of the form 2. In some minutes the stationary state is then attained also in this case and then, later, the expression reduces to the simple form 8. By extrapolating this second part of the function to zero time, one has: $(x')_{t\rightarrow 0} = -A_2 + A_3$ and $(y')_{t\rightarrow 0} = 1 - (x')_{t\rightarrow 0} = 1 + A_2 - A$. Thus, the ratio

$$\left(\frac{x'}{y'}\right)_{t\rightarrow 0} = \frac{-A_2+A_3}{1+A_2-A_3} = k \quad . \quad . \quad . \quad (10)$$

represents, in this case too, the simple partition of ThB between the surface and the solution for the stationary state between the first crystal layer and the solution, *i.e.*, k has the same meaning as in the former case, according to eqn. 9′. With this value of k, the numerical value of w can be derived also for these more complicated systems by eqn. 9. Now, having the numerical value of w, one obtains the value of the " active portion " of the surface by eqn. 4, which can be written :

$$z/X = (\delta/D \, . \, X/F \, . \, 1/C) \, . \, w, \quad . \quad . \quad . \quad (11)$$

all quantities in the bracket being known.[15]

In Table VI. the results of the radioactive measurements have been summarised on the lines of eqn. 11, in comparison with the results of the direct adsorption measurements. It is seen that when the adsorption could be measured by direct concentration measurements, the results are in very good agreement with the number of active spots, derived from the radio-

TABLE VI.—The " Active Portion " of Surfaces of Lead Salt Powders.

Preparation.	" Active Portion " of the Surface—	
	By Direct Adsorption Measurements.	By Radioactive Method (Eqn. 9 and 11).
Lead iodide . .	about 10^{-2}	$2{\cdot}0 \times 10^{-4}$
Lead sulphate A .	about 10^{-2}	$1{\cdot}3 \times 10^{-3}$
Lead sulphate B .	about $1{-}5 \times 10^{-3}$	$0{\cdot}9 \times 10^{-3}$
Lead chromate .	$6{\cdot}67 \times 10^{-2}$	$4{\cdot}7 \times 10^{-2}$
Lead chromate .	$6{\cdot}67 \times 10^{-2}$	$4{\cdot}3 \times 10^{-2}$

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[14] In the paper,[13] this velocity is represented by the first of the expressions 11 (page 416). This expression is in general accord with the present experiments too, but a close discussion of the Paneth process may be left aside here.

[15] For D the known diffusion constant of lead nitrate, *i.e.*, 0·71 cm.²/day was taken. The thickness of the adherent solvent layer (δ) was found (*loc. cit.* to be $1{\cdot}03 \times 10^{-2}$ cm. at 0° C. and $0{\cdot}4 \times 10^{-2}$ cm. at 20° C. The solubilities (C) were determined partly by analytical methods and partly by the radioactive indicator method of G. Hevesy and F. Paneth, *Z. anorg. Chem.*, 1913, **82**, 313. (The values are given in Table V. in the heading.)

active measurements by the method of eqn. 9 and 11. The radioactive method, represented by these equations, seems therefore suitable for the determination of the active spots of the surface when the velocity of the recrystallisation is not too great.

As to the general applicability of the method, one further remark may be made. In seeking a suitable procedure for making lead sulphate powders of very large specific surface for direct adsorption measurements, it was first thought that solid lead acetate powder must be mixed with concentrated sulphuric acid in *much greater quantity* than corresponds to the lead acetate. Now, in this way a preparation was finally obtained, which adsorbed very large quantities of lead nitrate, so that the adsorption values seemed to indicate an " active portion " of about 3 per cent. of the surface. In contrast to this, the radio-active method of the eqn. 9 and 11, applied to the same preparation, gave only about $1 \cdot 5 \times 10^{-8}$ for the value of the " active portion." In order to clear up this discrepancy, the solutions of the adsorption systems were carefully examined and an appreciable quantity of $H^{\cdot}$ ions was found to have been liberated from the crystal by the " adsorbed " lead ions. The " adsorption " was therefore not a real adsorption of the Langmuir type, but an exchange reaction between the $Pb^{\cdot\cdot}$ ions of the solutions and the $H^{\cdot}$ ions present in the crystal mass as a result of the method of preparation (*i.e.*, because of the great quantities of sulphuric acid used).

It is seen from this that the radioactive method of eqn. 9 and 11 indicates only the real adsorption—according to the mechanism represented by Fig. 1—and thus it is suitable *for fixing quite sharply the limits of real adsorption*, in contrast to the direct concentration measurements, where such a separation of the phenomena often is not possible. This presents, in addition, great accuracy, a further advantage, from the standpoints of some problems of the surface phenomena (*e.g.*, stability of colloids, heterogeneous catalysis, etc.), in which the *real* adsorption play a considerable part.

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THE DIELECTRIC CONSTANTS OF ETHER-CHLOROFORM AND ETHER-CHLOROBENZENE MIXTURES.

By I. E. Coop.

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The problem of molecular association and of molecular compound formation in binary liquid mixtures has been the subject of a considerable amount of investigation. Of the physical properties studied, the vapour pressures, freezing points, viscosities, specific heats and heats of reaction have in the past been the chief ones used.

The dielectric constant now provides another and very powerful method of investigation, particularly since it is capable of giving a more definite physical interpretation of the results obtained. The most important of the various phenomena which may take place in a binary liquid mixture are dipolar association induced polarisation and formation of a co-ordinate link and all of these would have some measurable effect on the dielectric constant, displacing it from the ideal solution value in a direction depending upon which of the above effects predominates.

Earp and Glasstone,[1] have recently used this method to investigate a number of binary liquid mixtures at 20° C. The following work was carried out independently before that paper was published, and the conclusions arrived at confirm their results. Inasmuch as the following work not only confirms, but extends the observations over a large temperature range, it may be used to supplement their conclusions. The ether-chloroform system was investigated, since considerable work had already been done on the other properties of the system. Wyatt's work,[2] on the freezing-points of the ether chloroform system has shown evidence for the existence of four compounds, (i) a comparatively stable equimolecular compound $(C_2H_5)_2O \cdot CHCl_3$, m.p. — 91·6° C., (ii) a compound $(C_2H_5)_2O$ $2CHCl_3$, stable only in excess of ether at the melting-point, and (iii) and (iv) two unstable compounds $2(C_2H_5)_2O \cdot CHCl_3$, and $3(C_2H_5)_2O \cdot CHCl_3$. He explained their formation as due to co-ordination between the oxygen atom and the chlorine atoms. To test this view the ether-chlorobenzene system, upon which very little work has been done was also selected for investigation. Earp and Glasstone concluded from the reduction of association or compound formation when the hydrogen of chloroform was substituted by a halogen that the oxygen atom of the ether co-ordinates, not with the halogen atoms but with a suitably activated hydrogen atom.

Purification of Materials.

Ether, commercially pure, was left over sticks of caustic soda, washed with concentrated caustic soda solution, left over caustic soda sticks again and dried with calcium chloride. It was then distilled and left over sodium wire and freshly distilled as required.

Chloroform, A.R., was dried over phosphorous pentoxide and distilled as required, the fraction boiling between 61·1° C. and 61·2° C. being taken.

Chlorobenzene was purified by shaking several times first with concentrated sulphuric acid and then with water, dried over fused calcium chloride and then distilled.

The purity of these liquids was confirmed before use by the measurement of the refractive index.

Apparatus and Experimental Procedure.

Density.—A dilatometer with arms of capillary tubing, was used. The bulb was immersed in the bath liquid and the levels in the arms measured by means of a cathetometer. The dilatometer was calibrated with ether and the coefficients of expansion of the pure components and some mixtures were measured over the range + 20° C. to — 80° C. From Thorpe and Rodger's values,[3] of the densities of ether chloroform mixtures at 0° C. and from values obtained experimentally by means of a pyknometer for the ether chlorobenzene system the densities of any mixture at any temperature could be obtained graphically.

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[1] Earp and Glasstone, *J. Chem. Soc.*, 1935, 1709.

[2] Wyatt, *Trans. Faraday Soc.*, 1929, **25**, 43.

[3] Thorpe and Rodger, *J. Chem. Soc.*, 1897, 370.

Refractive Index was measured at 16·9° C. and 5·4° C. by means of an Abbé refractometer. The molecular refractions calculated gave smooth curves showing no anomalies.

Dielectric Constant.—The heterodyne beat method was used. The apparatus (Fig. 1) consisted of a constant frequency oscillator I., another oscillator II. containing the experimental cell and standard variable air condenser and a detector and receiver III. containing an oscillating detector. Oscillators I. and II. have electron coupled screen grid valves type 24A (American) which in the circuit used maintain oscillations of constant frequency. The advantage of the oscillating detector is that it is a simple yet very sensitive method of detecting the beats between oscillators I. and II. When the fundamental of one is used against different harmonics of the others there is no detrimental interaction. The frequencies used in the oscillators were I. 90 kilocycles ; II. 360 kc. ; III. 2990 kc., approximately. Oscillator II. is tuned to give zero beat with the fourth harmonic of I. Constant frequency in oscillator III. is not necessary since the beat note heard in the loudspeaker is that between I. and II. The various parts of the apparatus were shielded by earthed metal containers. The standard variable air condenser A was one of 1250 μμF, Type IIB made by Muirhead Ltd., calibrated correct to two parts in 10,000, and allowing of a determination to ·1 μμF. As this was not large enough for the larger dielectric constants a shielded, fixed air condenser B of 1159·4 μμF was included in the circuit.

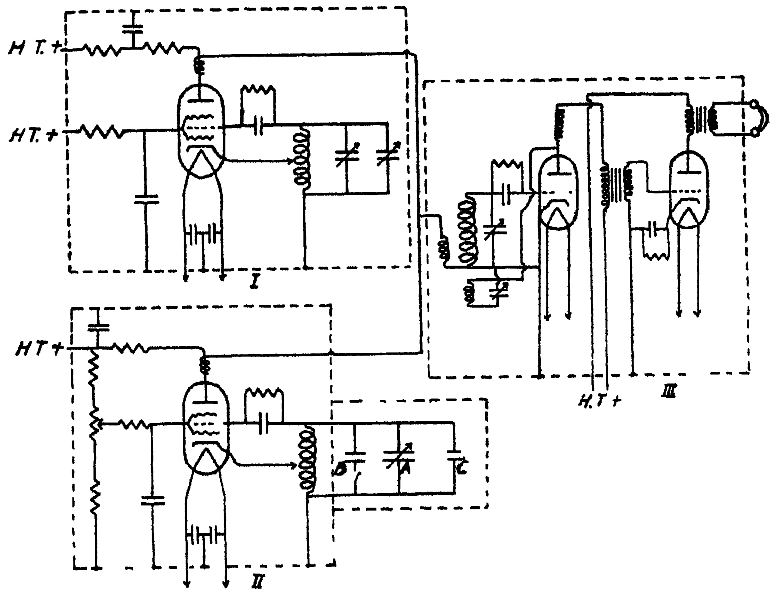


Fig. 1.

The test condenser or cell C was made of three concentric brass cylinders the middle live one being held between the other two by means of small blocks of mica. The latter two were held together at the top and bottom by threaded rings through which holes were bored for circulation of the liquid. The live cylinder was 13 cms. long and 1·8 cms. in diameter. A closely fitting copper container and mica lid enclosed the cell to which a brass support and lead was soldered. The liquid was held in the container and completely covered the cell.

The cell was calibrated at + 20° C. with pure benzene, the total capacity in air being 171·5 $\mu\mu$F of which 4·9 $\mu\mu$F was non-replaceable. The correction due to inductance of the leads had also to be determined, this being given by the relation $C_{\text{measured}} - C_{\text{true}} = l\omega^2 C^2$, amounting to 1·3 $\mu\mu$F at 1000 $\mu\mu$F.

Bath temperatures were measured by means of a platinum resistance thermometer, calibrated at + 100° C., 0° C., − 63·3° C. (melting-point of chloroform) and − 116·2° C. (melting-point of ether), and could be read off to ·1° C.

The bath consisted of ether (pentane for temperatures below − 100° C.) in a Dewar flask. This was cooled or frozen by means of liquid air and kept well stirred throughout the experiment. The cell was placed in the bath liquid and corresponding values of capacity and bath temperature were taken as the latter gradually rose. The rate of rise of temperature was 1° C. in two to three minutes at − 100° C.

The dielectric constants of the solids were determined after all the liquids had been done as it was feared that solidification and melting might change the capacity of the cell, but the largest change observed was only ·2 $\mu\mu$F, and the dielectric constants obtained were quite reproducible.

Results.

In Table I. are given the densities obtained experimentally. Owing to the difficulty of reading off from graphs and to possible sources of experimental error the densities are given to the third place only. Concentrations are expressed in molecular percentages of the second component, (chloroform or chlorobenzene).

TABLE I.

Temperature.	Pure Ether.	Pure $CHCl_3$.	72·33 Per Cent. $CHCl_3$.	50 Per Cent. $CHCl_3$	33·4 Per Cent. $CHCl_3$.	Pure C_6H_5Cl.	34·7 Per Cent. C_6H_5Cl.	47·2 Per Cent. C_6H_5Cl.	67·9 Per Cent. C_6H_5Cl.
+ 20° C.	0·7138	1·488	1·245	1·066	0·941	1·106	0·859	0·913	0·990
0° C.	0·736	1·526	1·277	1·095	0·967	1·127	0·882	0·935	1·012
− 20° C.	0·759	1·563	1·309	1·124	0·993	1·148	0·903	0·957	1·033
− 40° C.	0·781	1·602	1·343	1·153	1·020	1·170	0·926	0·979	1·055
− 60° C.	0·804	1·641	1·377	1·184	1·048	(1·192)	0·950	1·003	1·078
− 80° C.	0·828	(1·682)	(1·413)	1·215	1·076	(1·215)	0·977	1·028	(1·103)

(Extrapolated values are bracketed.)

Dielectric Constant.—For each mixture about twenty or more readings were taken over the temperature range from about − 80° C. to + 25° C. These were plotted on a very large scale, giving smooth curves from which the values in the Tables II. and III. were obtained.

TABLE II.—The Ether Chloroform System.

Temperature.	Pure Ether.	8·22 Per Cent.	16·06 Per Cent.	39·99 Per Cent.	50 0 Per Cent.	55·04 Per Cent.	60·0 Per Cent.	66·3 Per Cent.	81·15 Per Cent.	90·94 Per Cent.	Pure Chloroform.
+20° C.	4·300	4·630	4·975	5·762	5·981	6·009	5·983	—	5·600	5·265	4·785
0° C.	4·706	5·121	5·495	6·465	6·705	6·745	6·704	6·585	6·175	5·750	5·172
−20° C.	5·180	5·695	6·121	7·292	7·596	7·645	7·578	—	6·865	6·345	5·601
−40° C.	5·791	6·405	6·882	8·278	8·620	8·695	8·615	—	7·705	6·991	6·095
−60° C.	6·545	7·305	7·822	9·533	9·965	10·055	9·915	9·720	8·765	7·802	6·772
−80° C.	7·541	8·44	9·035	11·05	11·635	11·755	11·515	11·40	—	—	—

TABLE III.—THE ETHER CHLOROBENZENE SYSTEM.

Temperature.	Pure Ether.	19·65 Per Cent.	39·5 Per Cent.	50·0 Per Cent.	61·0 Per Cent.	79·2 Per Cent.	Pure Chlorobenzene.
+ 20° C.	4·300	4·615	4·935	5·075	5·205	5·400	5·605
0° C.	4·706	5·015	5·285	5·441	5·582	5·783	5·982
− 20° C.	5·180	5·469	5·745	5·870	6·005	6·205	6·401
− 40° C.	5·791	6·005	6·255	6·365	6·481	6·655	6·872
− 60° C.	6·545	6·655	6·845	6·960	7·050	—	—

Dielectric Constants of Solids.

The dielectric constants of the solids measured are given in Table IV. Only the temperature ranges over which they are practically constant are given. Owing to the fact that the cell was not thermostatted the values obtained where the dielectric constant increases rapidly near the melting-point, are not reliable so these are not given.

TABLE IV.

Solid.	Dielectric Constant.	Temperature Range.
Ether	2·27	− 141° C.— 127° C.
Chloroform . . .	2·61-2·69	− 190° C.— 120° C.
33 per cent. Chloroform .	2·81-2·85	− 128° C.— 123° C.
50 per cent. Chloroform .	2·23	− 140° C.— 125° C.
66 per cent. Chloroform .	2·51	− 123° C.— 113° C.
Chlorobenzene . . .	2·74	− 75° C.— 60° C.

Discussion of Results.

The dielectric constant composition curves for the ether chloroform system shown in Fig. 2 show the existence of a definite maximum which becomes more pronounced as the temperature decreases. The maximum occurs at 55 per cent. chloroform indicating the formation of the equimolecular compound, the amount increasing at low temperatures as would be expected. The deviation from the smooth curve just noticeable at − 60° C., becomes quite appreciable at − 80° C., and is probably due to the formation of a certain amount of the compound

$$(C_2H_5)_2O \, . \, 2CHCl_3.$$

The polarisation curves calculated from the formula $P = \frac{\epsilon - 1}{\epsilon + 2}\frac{M}{D}$ where $M = C_1M_1 + C_2M_2$, no account being taken of compound formation, lead to the same conclusion the maximum deviation being at 50 per cent. chloroform. In order both to produce the maxima and to counteract the decrease in the number of resultant dipoles the dipole moments of the compounds must be large. Assuming complete compound formation at the melting-point, the minimum values of the dipole moments found by the optical method are 1·55 and $2{\cdot}0 \times 10^{-18}$ e.s.u. for $(C_2H_5)_2O \, . \, CHCl_3$ and $(C_2H_5)_2O \, . \, 2CHCl_3$, calculated from the polarisation of the pure liquid. The moment at infinite dilution in some non-polar medium must certainly be considerably greater than this.

Earp and Glasstone have calculated the polarisation of the compound $(C_2H_5)_2O . CHCl_3$ by extrapolation of corrected polarisations of ether in chloroform to infinite dilution. In the present work sufficiently dilute solutions were not measured to enable a complete confirmation of their values, but there was agreement over the concentrations used The corresponding curves for the ether chlorobenzene system (Fig. 3) are distinctly different, being quite normal, indicating the absence of any type of compound formation involving co-ordinate links or of any tendency towards the formation of a less polar association complex.

These results are quite in accordance with the view that the formation of such molecular compounds takes place by the formation of a link between the oxygen atom of the ether and a hydrogen atom of the other component when that hydrogen atom is suitably activated by the proximity of a suitable electric dipole. The very limited existence of the compound $(C_2H_5)_2O . 2CHCl_3$, shows that there is some but very little tendency of the oxygen atom to form two co-ordinate links. The non-existence of any compound formation of ether with chlorobenzene finds an explanation only on the above theory, for the chlorine does not co-ordinate and the hydrogen atoms are not sufficiently activated.

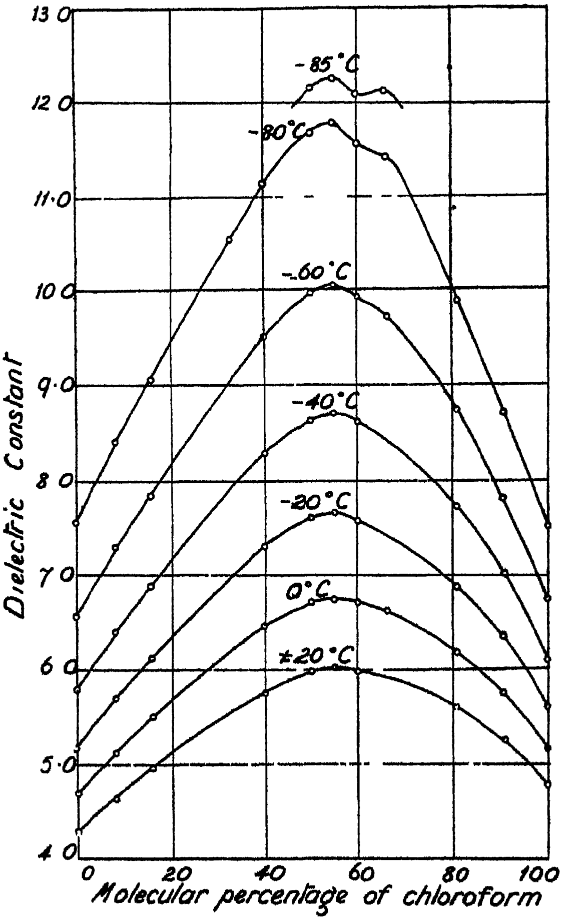
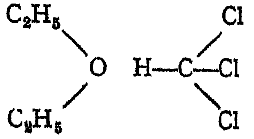


FIG. 2.

The ether chloroform compound is probably formed as Earp and Glasstone suggest by resonance between the two parent states



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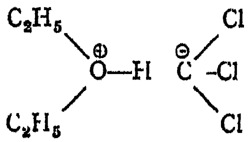

This hydrogen bond can only be formed when the hydrogen is initially attached to a strongly electronegative grouping and when the oxygen having donor properties is also strongly electronegative. The presence of three C—Cl bonds adjacent to the hydrogen in chloroform giving the C—H bond considerable ionic character and the presence of electron repelling alkyl groups in ether satisfy these conditions. Then in either of the alternative parent structures there are not pure covalent but hybrid covalent ionic links. In order to get stabilisation by resonance between these structures it is necessary for the oxygen and carbon atoms in the O--H--C system to come considerably closer together than is possible with free molecules of ether and chloroform and this can only take place when this process does not involve too much energy. For purely covalent bonds therefore this cannot take place readily since too much energy would be required to bring the system into such a state that it might be stabilised by resonance. When the bond has considerable ionic character however, the energy required is less and the system as a whole can be stabilised by resonance energy and by energy of electrostatic attraction. In chloroform the C—H link has ionic character $\overset{\ominus}{C}$—$\overset{\oplus}{H}$ and so the ionic parent structure would have appreciable stability having an energy similar to that of the other parent structure so that resonance can occur. Whenever atoms or groups which are attached to the carbon atom of a C—H bond increase the ionic character of that bond then they will promote the formation of a resonance linkage through the hydrogen with suitable donor atoms such as oxygen or nitrogen. In this way both the qualitative and quantitative results of the extent to which molecular compounds of this type are formed can be given an explanation.

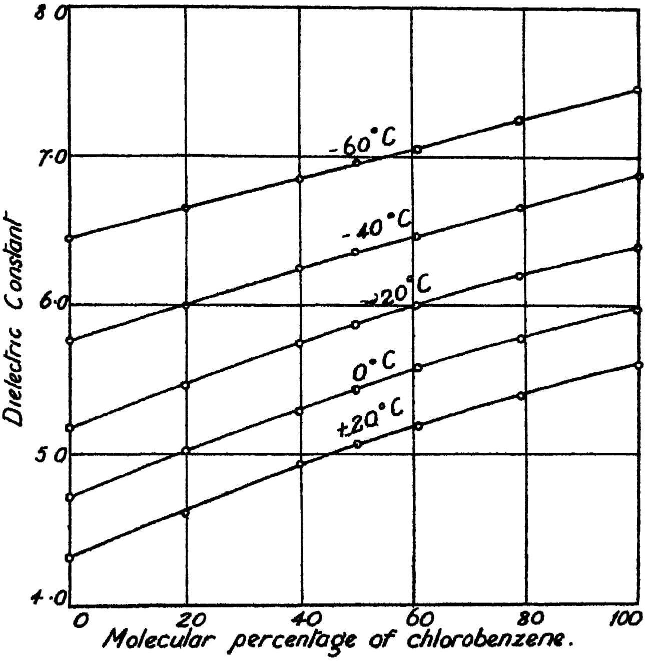

FIG. 3.

Summary.

This dielectric constant work was carried out to obtain some idea of the extent of compound formation in the ether chloroform system as other properties indicated that a compound existed to a considerable extent in equilibrium with the pure components. By investigation at low temperature it was considered that the anomalous behaviour would become more distinct. The results obtained were not amenable to accurate quantitative estimations of the extent of the compound formed but certain conclusions could be derived concerning the nature and structure of the compound. They indicated that the oxygen atom of ether co-ordinates not with the halogen atoms but with the hydrogen atom of the chloroform. The possible nature of this new link is discussed.

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THE PHOTO-ELECTRIC SCHOTTKY EFFECT IN FILMS OF SODIUM AND POTASSIUM ON TUNGSTEN.

By R. C. L. Bosworth.

Received 3rd December, 1936.

The theory[1] for the lack of true saturation in a thermionic tube leads to the following equation for the change in thermionic current (I) drawn from a cathode under the influence of a field F in volts per centimeter, at a temperature T:—

$$\frac{d \log I}{d\sqrt{F}} = \frac{1{\cdot}906}{T}. \qquad . \quad . \quad . \quad . \quad . \quad (1)$$

This equation holds admirably for emission from clean metals[2, 3] while for contaminated metals $d \log I/d\sqrt{F}$ is much larger and is not independent of F. Application of the Schottky effect to photo-emission has been made by Lawrence and Lingford,[4] Ives,[5] and Suhrmann,[6] and as a result it is realised that thick films and pure metals give a red shift of the photo-threshold with increasing field of approximately the magnitude required by Schottky's theory while for thin films the variation of current with field is much more pronounced.

Two theories have been propounded to account for the very poor

[1] Schottky, *Z. Physik*, 1923, 14, 63.
[2] Pforte, *ibid.*, 1928, 49, 46.
[3] de Bruyne, *Proc. Roy. Soc.*, *A*, 1928, 129, 423.
[4] Lawrence and Lingford, *Physic. Rev.*, 1930, 36, 482.
[5] Ives, *Astrophy. J.*, 1924, 60, 209.
[6] Suhrmann, *Naturwiss.*, 1928, 16, 336.

saturation of dilute films. Becker and Mueller[7] build their theory around the positive grid hypothesis.[8] They imagine the adsorbed layer producing a meshwork of positive ions over the surface. The existence of this grid produces an acceleration on an electron near the surface and retards it at greater distances; and the Schottky effect is abnormal because the long range field is not an image field. For this theory to be valid, however, the field due to the positive grid must extend over a distance of the order of a hundred atomic diameters (the order of the distance at which a normal external field becomes comparable with the image field); this is difficult to reconcile with experiments such as those of Nottingham[9] which show from unsaturation current measurements that the potential hump produced by a film of thorium on a tungsten surface is only of atomic dimensions in width; so that we turn to the second theory of poor saturation—the theory of patches developed by Langmuir.[10] This regards the dilute adsorbed film not as spread uniformly over the surface, but as occurring in localised patches of high concentration; between the patches of high and low concentration considerable local fields are set up and these fields are of such a sense as to repress the emission from the patches of lower work function. The application of the external field by neutralising the local fields facilitates the emission from these active patches, and so produces a nett increase from the whole surface which is in excess of that produced by a uniform field of the same concentration acting on a homogeneous surface.

In the author's work[11, 12] on films of sodium and potassium on tungsten, certain indications of inhomogeniety in the film properties emerged. It was found, for example, that a dilute film of potassium formed by condensation was relatively immobile at room temperature while concentrated films were quite mobile. If now a dilute film be formed from a concentrated film by cautious evaporation, it will retain to a large extent the high mobility of its parent film. One is accordingly led to postulate that the two states of the surface, before and after establishing the continuous film, correspond to two different phases, and that the initial dilute film of low mobility is labile or metastable, so that once the concentrated mobile film becomes established it exhibits a certain amount of stability, and when broken up by removal of potassium, tends to persist in the form of small localised patches—large enough as a whole to make the film only feebly photo-active, but numerous enough to make it uniformly active when measured by a spot of light of two square millimeters area. These concentrated patches are to be imagined as continuous along the strip, forming a meshwork all over the surface and so imparting to any additional deposit the high mobility proper to their own local high concentrations; although the average concentration for the whole surface may be quite low. A natural choice for the position of these veins of concentrated film is that of the crystal edges and cracks, which form such a meshwork as that required by the high mobility recorded by experiments, and at which, since they are to act as paths from the surface to the inner structure, it is natural to look for localised banking up of the potassium. In the experiments on sodium where no evidence for surface migration was obtained until all the inner surface was full, it is reasonable to suppose that these veins of high concentration were always present, and by providing an easy path over the surface accounted for the high mobility of the sodium.

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[7] Becker and Mueller, *Physic. Rev.*, 1928, **31**, 431.
[8] Becker, *Trans. Amer. Electrochem. Soc.*, 1928, **55**, 153.
[9] Nottingham, *Physic. Rev.*, 1932, **41**, 793.
[10] Langmuir, *Gen. Elec. Rev.*, 1920, **23**, 504.
[11] Bosworth, *Proc. Roy. Soc., A*, 1935, **150**, 58.
[12] *Ibid.*, 1936, **154**, 112.

The surface diffusion properties of the various films studied before, have accordingly been tested in the light of Langmuir's patch theory of the Schottky Effect.

Apparatus and Calibration.

The apparatus employed varied but little from that used in the work of surface diffusion.[11, 12] The grid, however, was replaced by a set of three coaxal cylindrical anodes, slotted in front, to permit admission of the light. These cylindrical anodes would, it was hoped, give a more uniform field at the central ribbon filament than a simple grid. The actual variation in emission finally obtained will depend on the field at the filament and this, although directly proportional to the voltage on the anode, will depend also on the geometry of the tube. Since the filament is rectangular in cross-section, while the cross-section of the anode is circular the field at the filament cannot be uniform and will be more intense at the edge than on the flat faces. It is a little difficult to see just what average field this actual field will be equivalent to, and so the effective field was determined experimentally by measuring the current-volts characteristic of a clean filament and applying to it the results of the Schottky relation—Equation (1). The thermionic emission to the central anode with the outer two used as guard rings to eliminate end effects due to conductance of the leads was accordingly measured at a fixed filament temperature and at various anode voltages (V) from 8 up to 210 volts, and the results obtained are shown graphically in Fig. 1 which shows log I plotted against V. The two different temperatures of 1665° K. and 1540° K. were used, and the unit of I in the two curves has been made different in order that they should both appear on the same graph. It will be seen from Fig. 1 that once the space charge effects have been overcome the Schottky relation does indeed hold, and at 1665° K,

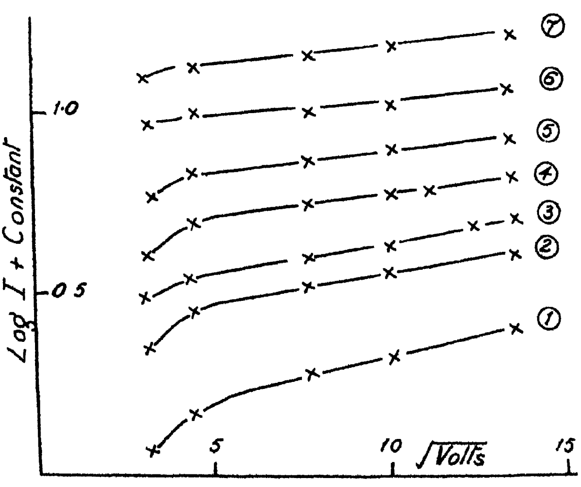

Fig. 1.

$$\frac{\mathrm{d} \log I}{\mathrm{d}\sqrt{V}} = 0{\cdot}008$$

or

$$T\frac{\mathrm{d} \log I}{\mathrm{d}\sqrt{V}} = 13{\cdot}2$$

And at 1540° K.

$$T\frac{\mathrm{d} \log I}{\mathrm{d}\sqrt{V}} = 0{\cdot}0065$$

or

$$T\frac{\mathrm{d} \log I}{\mathrm{d}\sqrt{V}} = 10{\cdot}0$$

The mean value of $T\mathrm{d}\log I/\mathrm{d}\sqrt{V}$ may thus be taken as 11·6 and when this is compared with the Schottky relationship, *viz.*:

$$T\,\mathrm{d}\log I/\mathrm{d}\sqrt{F} = 1{\cdot}9$$

it will readily be seen that V volts on the anode produce an effective field of $36V$ volts/cm. at the filament, this may be compared with the average field of $16V$ volts/cm. calculated from the geometry of the electrode system.

Results.

We now examine the saturation properties of the emission from contaminated tungsten. A dilute film of sodium was formed on the filament and the temperature raised until appreciable thermionic emission was produced and then the current-volts characteristic was measured, the temperature raised again and another set of measurements of the current at different anode volts obtained and so on. Fig. 2 expresses the emission for a fixed field at different temperatures, as usual log I/T^2 being plotted against $10{,}000/T$. The strip originally was covered with a dilute film of sodium and on heating gave a high emission until the temperature reached 1500° K., at which point the last trace of sodium evaporated and the emission from then onwards corresponded to that of a tungsten surface. After heating above 2000° K., the filament was allowed to cool and a straight line was obtained for the emission curve—all the sodium had been lost.

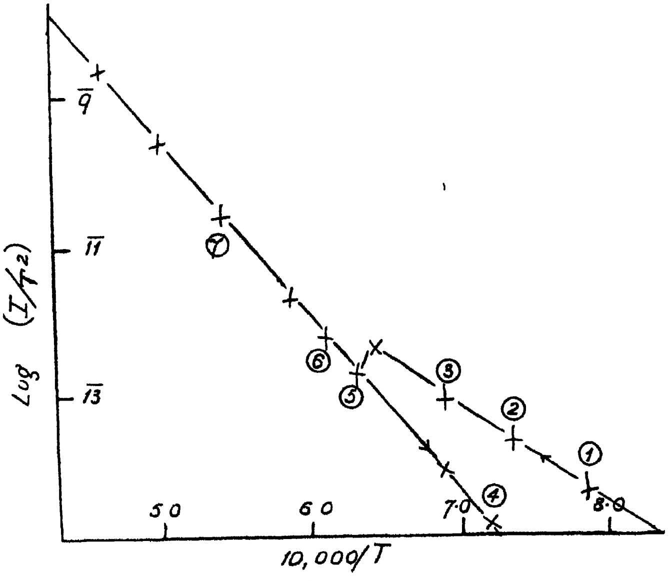

FIG. 2.

The current-volts characteristic for each of the seven points marked with a number has been measured and these are shown in Fig. 3 where log I is plotted against $\sqrt{V}$ for each of these seven points. The values of I are given on different scales in order to make them all fit the same graph. From Fig. 3 the slopes have been read off and the Schottky constant $T\mathrm{d}\log I/6\mathrm{d}\sqrt{V}$ determined. The results of this determination are given in Table I. and show that the Schottky constant is abnormal whenever there is any enhancement of the normal emission due to a sodium film. Indeed point (4) which appears on the clean tungsten line has a Schottky constant which is appreciably larger than the clean surface value. We should expect however, that any sodium that was not entirely removed from the neighbourhood of the surface—either by occlusion in the filament or condensation on the anodes or leads could begin to build up a film under the conditions attained when point (4) was recorded, *viz.*: cooling to 1400° K. after heating above 2000° K. If such a film had been produced it was too dilute to increase the thermionic emission above the limit set by experimental error, but not too dilute to produce an appreciable increase in the Schottky constant. In short a very dilute film commences to affect the saturation properties of the filament before it effects the emission. The variation in the photo-emission with applied voltage has also been recorded with this same apparatus. White light was used to illuminate the filament at 295° K. and the photo-emission measured at various anode voltages. Table II.(*a*) gives figures obtained for a dilute film of sodium on tungsten from which $T \mathrm{d} \log I/\mathrm{d}\sqrt{F} = 4{\cdot}0$, a figure practically identical with that obtained from thermionic measurements on dilute films of sodium.

TABLE I.

Point.	Temperature.	$T\mathrm{d}\log I/\mathrm{d}\sqrt{F}$.
1	1265	5·7
2	1350	3·4
3	1450	3·7
4	1400	2·5
5	1580	1·8
6	1630	1·6
7	1850	2·0

In the case of the more stable films of potassium the photo-electric Schottky effect has been measured under different conditions. With dilute films formed by condensation and exhibiting low mobility, the

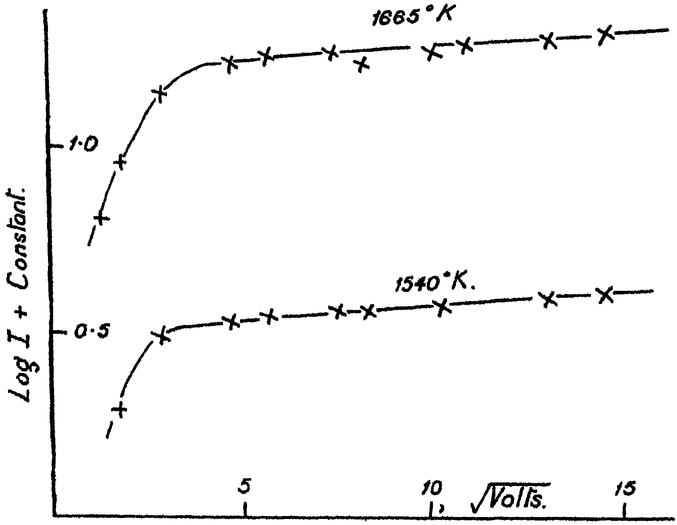

Fig. 3.

variation of emission with anode volts shown in Table II.(*b*) was obtained from which $T\mathrm{d}\log I/\mathrm{d}\sqrt{F} = 1{\cdot}0$.

When however, this concentrated film was partly removed by evaporation the dilute film which remained, and which differed from the dilute film above by its higher mobility, gave the emissions shown in Table II.(*c*) from which $T\mathrm{d}\log I/\mathrm{d}\sqrt{F} = 12$.

These results may be most naturally interpreted by saying that the microscopic structure was homogeneous in the second type of film, while in the first and last cases it was exceedingly patchy, a property already suggested as accounting for the high mobility over such a film; it is thought that these films may consist of veins rich in alkali forming a meshwork over the surface and the Smekal cracks [11, 13] have been suggested as natural localities at which these veins may occur. This suggestion is supported by electrostatic and chemical considerations as may be seen by the following treatment.

TABLE II.

Anode Volts V.	Photo-Electric Emission I (Arbitrary Units).
(a) Sodium:	
100	7·6
80	6·0
60	5·1
40	3·2
(b) Potassium:	
215	2·6
148	2·3
100	2·2
60	1·9
10	1·5
(c) Potassium (evaporated):	
100	4·0
90	3·5
80	2·5
70	1·5
60	0·8

If one considers a uniform plane cloud of positive ions at a small distance from a parallel metal surface which is however broken up into innumerable separate crystal blocks separated by fissures, it is clear that the positive cloud will produce a negative image cloud in the metal surface, but this image will not be homogeneous and will be of such distribution as to cause the lines of electro-static force to crowd together at the crystal edges, as shown in Fig. 4; so that if each ion be allowed to move adiabatically up to the surface it will come up along the lines of force, and we will have a distribution on the surface in which the film is most concentrated at the edges of the cracks, and least at the centre of the crystal faces. Provided the film is not sufficiently concentrated for repulsive spreading forces to come into play, this will be the equilibrium distribution and a film fired on in an homogeneous beam will, if it be mobile, tend to move until it attains this non-homogeneous distribution.

Chemical considerations of the block metal surface lead to similar conclusions. Foreign atoms or molecules may be adsorbed at the metal surface because each lattice atom at the surface has one unsaturated chemical valence. At the crystal edge, however, each lattice atom along the line of the edge must have two unsaturated chemical valences and therefore a much stronger tendency to tie onto foreign atoms, with the result that the position of minimum energy for any adsorbed layer insufficient to cover the whole of the surface will be one in which the adatoms are strongly concentrated at the crystal edges.

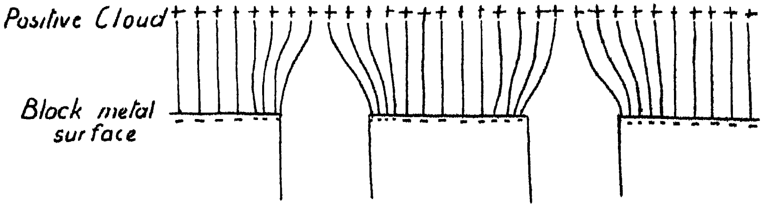

FIG. 4.

Summary.

(1) In a study of the surface diffusion coefficients of potassium it has been found that whereas dilute films formed by condensation have a low mobility, concentrated films and dilute films formed from them by

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[13] Smekal, *Physik. Z.*, 1928, **26**, 707; *Z. Physik*, 1927, **45**, 869, Zwicky, *Proc. Nat. Acad. Sci.*, 1929, **15**, 253.

evaporation have a high mobility. It is therefore suggested that this last type of film consists of veins rich in alkali forming a meshwork over the surface.

(3) The variation of the photo-electric emission under white light for the three types of film above has been studied—for the first two types of the film the variation is in accordance with the Schottky theory—for the last the variation is far greater and this points to the very inhomogeneous nature of this film.

(4) The variation of both thermionic and photo-electric emission from dilute films of sodium has also been studied and the films give a Schottky coefficient (T(d log I/d$\sqrt{F}$) of from two to three times the normal value calculated from the image field of an electron escaping from the surface.

It is a great pleasure to thank Professor E. K. Rideal for his continual interest in this work, and the Royal Commissioners of the 1851 Exhibition for a Senior Studentship.

Laboratory of Colloid Science,
Cambridge.

REVIEWS OF BOOKS.

Annual Tables of Constants and Numerical Data: Numerical Data on the Raman Effect: Spectra, Intensities, Modes of Vibration. By Dr. M. Magat, Collège de France (Reprint from Vol. XI. Years 1931-1934. **Numerical Data on Radioactivity, Nuclear Physics, Transmutations, Neutrons, Positrons.** By. I. Joliot-Curie, B. Grinberg, R.-J. Walen. **Numerical Data on Rotatory Power.** By E. Darmois. Published by Gaultier-Villars et Cie, Paris.)

The rapid growth of the technique of the determination of the Raman effect and its application to questions of molecular structure, together with the recognition that it is by a combined consideration of such data with those obtained in the infra-red region of the spectrum that conclusions of value as regards structure can be obtained, has made such a collection as this imperative for workers in this field.

Dr. Magat, in compiling the summary, which is divided into three parts, dealing with inorganic and organic substances, and a third on modes of vibration, has employed a critical feature, instead of quoting simply all results obtained by the workers. Thus he chooses as fundamental (Raman) spectrum the most complete one available, if necessary supplementing it by the data of others, and he prints in bold type lines found by at least two authors independently. On the question of intensity, difficult to assess on account of diversity of exposure, he uses his judgment, working downwards from an intensity of 10, with special attention to intensities of the fundamental spectrum.

It is, of course, difficult in making such a collection as this to include all references to Raman spectra that have appeared when the titles of papers do not indicate specific treatment of this feature, and the writer thinks he has found at least one such omission, but nevertheless, the collection and bibliography appear to cover the field and it includes a very large number of substances. Thus a rough calculation of the substances whose Raman spectra are tabulated in the section dealing with organic substances is no less than 1200.

Dr. Magat has also written a part dealing with the modes of vibration of polyatomic molecules, and this is accompanied by a useful bibliography of theoretical papers on this subject. This part is illustrated by diagrams which show the direction and disposition of the forces involved, and it indicates when those modes of vibration are to be attributed to infra-red or to Raman frequencies, quoting in each case examples of the compounds concerned. There is an English as well as a French text.

This collection of considered data will prove very useful to workers in this field, and so rapid is the advance in it, that an extension up to the present date will soon be necessary. R. R.

The collection of data on nuclear physics will be found to be of the greatest use to all workers in this field. It covers the period from 1931 to April, 1936, and is divided into two sections, A: Natural Radioactivity; and B: Transmutations, Artificial Radioactivity, Neutrons and Positrons. Section A contains recently acquired information about periods, α-, β- and γ-rays. Section B on transmutations is a remarkable compilation, both for its completeness and the ease with which it may be used. First there is a table comprising the transmutations of the elements of atomic number 1 to 30 by various bombarding particles, with the data on yields, energies of emitted particles, γ-rays and energy balances. Table II. deals with the radio elements from the first thirty elements, both as regards their formation and the details of their disintegration. Table III. treats separately the elements of atomic number 31 to 92. This division is justified, since there is here far less detailed information available and the complication of the data is extreme. Finally, there is a bibliography on the passage of neutrons through matter, a table of the stable isotopes, data and bibliography on the production of positrons, and a range-energy table for protons. The book is printed both in French and English, mostly in parallel columns, with the numerical data in the centre. Skilful arrangement prevents this becoming at all cumbersome.

The literature of the subject of transmutations has grown so greatly in the last few years that this well-arranged collection of data with a complete bibliography will prove of real service to the subject, and will amply repay the great trouble it must have given the authors to produce. C. D. E.

The third volume contains the data on rotatory power published in the years 1931 to 1934 and classifies them under the headings (i) rotatory power of substances in the homogeneous state and in solution, (ii) effect of temperature, concentration and solvent on rotatory power, (iii) rotatory dispersion, (iv) resolution of racemic compounds, (v) mutarotation, (vi) effects due to the addition of a third substance to a solution of an optically active compound, (vii) references to the literature dealing with general theories, including those bearing on Walden inversion, configuration, absorption, optical superposition, asymmetric synthesis.

The total number of references is 390. J. K.

Physik und Chemie. Part I.: Magnetochemie. By W. Klemm. Akad. Verlags. m. b H. (Leipzig, 1936. Pp. xiv and 262. Price RM. 16. Bound RM. 18.)

The later developments of quantum mechanics have tended to make the presentation of subjects with which they are primarily concerned rather forbidding to the practitioner trained in the aims and methods of the older school. It need not be so; it is possible to concentrate attention on the results, rather than on the minute details of the methods of modern analysis, and Professor Klemm's book is an excellent example of well-balanced treatment. He begins at the very beginning, his first section dealing with the elementary phenomena of the magnetic field, and with methods of measurement. The second section (magnetic moment and atom-theory) deals briefly with the work of Curie and the theories of Langevin and Weiss, and proceeds to an exposition of the applications of the older quantum theory and of quantum mechanics. The third main section is devoted entirely to applications to chemical problems.

The volume is clearly written, is well-documented, and may be recommended as a trustworthy introduction to the subject.

A. F.

Wireless Engineering. By L. S. PALMER. (Longmans, Green & Co. Ltd. London. Pp. xii and 544. Price 21s. net.)

This volume is in effect the second edition of the author's *Wireless Principles and Practice* (1927), but owing to the considerable changes from the original text it is given a new title. The book is intended for students preparing for university degrees, and to meet the requirements of electrical engineers who wish to become conversant with wireless. It is suited for such readers, and contains a reasonably up-to-date outline of the principles of the subject.

As a general text-book for reference purposes, however, the book is a little disappointing—not so much in the matter as in the mode of presentation. A book of this standard is often useful to the general reader who already knows something of the subject, but does not normally concern himself with it in his vocation; he wishes, however, to possess an up-to-date text-book for purposes of reference. He has forgotten, say, what is the " three-halves-power law," but, although the book would tell him, the index will not help him to find the answer. Again, although the author makes brief reference in the text to " Class B " amplification, there is no clear reference to it in the index. The reviewer does not remember seeing any reference to the pentode; there is none in the index, and a hurried second survey of the diagrams fails to disclose it; there may be a paragraph tucked away in the text, but, for the general reader we have mentioned, it might as well be absent and, in the year 1936, that is surely a serious defect.

ABERDEEN: THE UNIVERSITY PRESS

THERMODYNAMICS AND THE VELOCITY OF IRREVERSIBLE PROCESSES.

By A. R. UBBELOHDE.

Received 22nd February, 1937.

Thermodynamic functions such as entropy and free energy or available energy are primarily defined in connection with reversible changes. Although a great variety of statistical methods has been developed for dealing with irreversible processes, thermodynamics does not normally include the time variable in its scope. Using the concept of dynamic equilibrium, attempts have recently been made to calculate the velocity of chemical change from thermodynamical considerations.[1, 2] The present paper discusses a more general method of applying the conditions for thermodynamic equilibrium to the calculation of the velocity of irreversible processes.

Rate of Change of Thermodynamic Functions, and Fluctuations in a System.

Under certain conditions, the maximum rate at which any thermodynamic function of a system can change is intimately connected with the fluctuations in the system, when in equilibrium. The theory of fluctuations shows that in any element of volume there is a finite probability that at any instant a thermodynamic property P shows a departure $P - \bar{P}$ from the average[3] value $\bar{P}$. The magnitude of this fluctuation will change with time. Thermodynamics can make no direct statement about the relaxation time of a fluctuation, which is a characteristic of the system depending on its statistical make up, and probabilities of transition between the different energy states. Information is nevertheless available about the average magnitude and general trend of fluctuations in a system, which can be used to obtain certain well-known results without detailed analysis.

The essential idea is that the readjustment of any thermodynamic function can only proceed in a direction predicted by the second law of thermodynamics. The rate of readjustment will normally be the same as the average rate of change of the local fluctuations about an equilibrium value. When the influence of temperature, pressure or any other variable on these fluctuations is known, their influence on the rate of irreversible processes involving the same fluctuations can be inferred.

Two typical processes which will illustrate the method to be adopted are the dissipation of electrical energy in metals, and the increase in entropy resulting from the conduction of heat. When a quantity Q of electricity passes from a potential V_1 to a potential V_2 in an irreversible

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[1] M. Evans and M. Polanyi, *Trans. Faraday Soc.*, 1936, 32, 1333.
[2] Moelwyn Hughes, *ibid.*, 1936, 32, 1723.
[3] R. Fowler, *Statistical Mechanics*, Cambridge, 1936, 743.

process, as in the conduction of electricity through metals, the available electrical energy dissipated is

$$Q(V_1 - V_2).$$

In order to complete the cycle, the same quantity of electricity may be brought by some reversible process back to the original potential. In the same way, in the conduction of heat, when a quantity Q of heat passes from temperature T_1 to temperature T_2 the entropy increase is

$$Q/T_2 - Q/T_1.$$

The cycle may be completed as before, by a reversible process, returning Q to a reservoir at the higher temperature.

Such processes can be made to take place in systems in the *steady state*, in which the temperature at any part is constant, and there is no accumulation of electricity or heat at any part. The second law of thermodynamics may be applied to the steady decrease of available energy, or steady increase in entropy per unit volume of the system, as follows:—

Thermodynamic Derivation of Ohm's Law.

According to the second law of thermodynamics, when the system considered is in equilibrium, the available electrical energy is a minimum, and fluctuations in A can only lead to a zero change, as is expressed by the equation

$$(\overline{A} - \bar{A}) = 0,$$

indicating that the probability of a fluctuation of A above $\bar{A}$ is equal to the probability of a fluctuation of A below $\bar{A}$. Whatever the detailed kinematics of a system may be, the value of A in any element of the system will on the average always tend to adjust itself to be the same as the average value of A for all the neighbouring elements, *i.e.*, the equilibrium or minimum value for the system under the conditions chosen. *The direction in which A must tend to change as the result of kinematic changes can be summed up in the statements that A tends to equality with the neighbouring elements, and that A tends to the minimum value.*

As soon as a gradient of available energy is set up in the system by some physical means, it is no longer possible to satisfy both these conditions for equilibrium, and some irreversible changes must take place as a result. When a fluctuation has taken place in any element of volume of the system, A has a somewhat bigger probability of returning to the average value $A - \frac{\partial A}{\partial x} \cdot dx$ of the element immediately below it on the gradient, than to the average value of the element immediately above it, $A + \frac{\partial A}{\partial x} \cdot dx$. At the present stage it is not necessary to analyse this probability more closely. When the gradient $\frac{\partial A}{\partial x}$ is small, so that changes of the second and higher orders $\frac{\partial^2 A}{\partial x^2}$, etc., may be neglected in a small region of the system, the rate at which A can change per unit volume will be some function of the gradient $\frac{\partial A}{\partial x}$, which may be expanded in a power series

$$\left(\frac{\partial A}{\partial t}\right)_{\text{unit volume}} = f\left(\frac{\partial A}{\partial x}\right) = a_1\left(\frac{\partial A}{\partial x}\right) + a_2\left(\frac{\partial A}{\partial x}\right)^2 + a_3\left(\frac{\partial A}{\partial x}\right)^3 \ldots$$

there being no term independent of $\left(\frac{\partial A}{\partial x}\right)$ since $\left(\frac{\partial A}{\partial t}\right) = 0$ in the absence of a gradient.

From the second law of thermodynamics, the coefficient a_1 must be zero, since otherwise by reversing the direction of the gradient A would increase spontaneously. For small gradients it is sufficient to retain the second term only of the expansion, so that the simplest possible thermodynamical equation for the dissipation of available energy in the steady state will be

$$\left(\frac{\partial A}{\partial t}\right)_{\text{unit volume}} = -K_a\left(\frac{\partial A}{\partial x}\right)^2,$$

where K_a is a constant depending upon the system considered. This equation is readily seen to be equivalent to Ohm's law.

$$\left(\frac{\partial A}{\partial t}\right)_{\text{unit volume}} = \frac{dQ}{dt} . \Delta V = C . \Delta V \quad \text{per unit volume,}$$

where C is the current $\frac{dQ}{dt}$, and in an element of volume of unit area and thickness dx, $\Delta V = \frac{dV}{dx}$. The available electrical energy A may be written eV, where e has the dimensions of a charge, and V is the potential. The thermodynamical equation thus transforms to

$$C\frac{dV}{dx} = K_a e^2\left(\frac{dV}{dx}\right)^2, \quad \text{or} \quad C = -K_a e^2 \frac{dV}{dx},$$

which is one of the ways of writing Ohm's law. It will be noted that the specific conductivity of a conductor is proportional to the constant $+K_a e^2$, and thus to the rate of dissipation of available electrical energy per unit volume, in the steady state.

It must be noted that this derivation of Ohm's law merely obtains it as the simplest thermodynamic equation for an irreversible process in the steady state, and does not indicate for what values of $\left(\frac{\partial A}{\partial x}\right)$ it would break down.

Temperature Coefficient of Electrical Resistance.

By making certain simple assumptions it is possible to discuss the temperature coefficient of electrical resistance in general terms, *i.e.*, on a quasi-thermodynamical basis instead of a statistical basis. The assumption is that the value of $\left(\frac{\partial A}{\partial t}\right)_{\text{unit volume}}$ is determined by the *average* value of the fluctuations at any temperature $|\overline{\delta A}|$. This assumption is equivalent to averaging the transition probabilities of the individual energy states of the system, and assuming that the average does not change appreciably with temperature. This requires *inter alia* that the fluctuations are independent of one another.

To a first approximation this assumption may be summed up by the equation

$$K_a = a|\overline{\delta A}|,$$

where a is a constant independent of temperature. In order to obtain comparable gradients at different temperatures, these must be written in the form

$$\frac{1}{\overline{\delta A}}\,\frac{\partial A}{\partial x}.$$

Combining these equations and applying the second law as before,

$$\left(\frac{\partial A}{\partial t}\right)_{\text{unit volume}} = -ae^2\,\overline{\delta A}\left(\frac{1}{\overline{\delta A}}\cdot\frac{\partial A}{\partial x}\right)^2,$$

where $-ae^2$ is a constant independent of temperature The simplest thermodynamic equation for the dissipation of available energy is thus

$$\left(\frac{\partial A}{\partial t}\right)_{\text{unit volume}} = -\frac{K}{\overline{\delta A}}\left(\frac{\partial A}{\partial x}\right)^2.$$

When the fluctuations in A are solely due to thermal equilibrium, and are independent of the fluctuations in internal energy E, the average value of δA may be obtained from Einstein's [1] theory.

Since $\qquad A = E - TS$

and E is constant, $\qquad \delta A = \quad T\delta S$

Using Boltzmann's relation $S = k \log W$, the probability W' of a fluctuation δA in any element of the system is

$$W' = We^{-\delta A/kT},$$

and the average value of $|\delta A|$ is

$$|\overline{\delta A}| = \left[\int_0^\infty \delta A\,.\,W'\right] \Big/ \left[\int_0^\infty W'\right] = kT.$$

Thus when the assumptions are valid the specific conductivity

$$\mu = b/T,$$

where b is a constant independent of temperature. It is of course well known that many pure metals show approximately this temperature coefficient at high temperatures, where the number of states is so large that the assumptions about the relaxation time are reasonable.

The same law will apply to a mixture of two pure metals, but a solid solution has an additional temperature independent term in the resistance, whose origin can only be illustrated by analogy in the theory of fluctuations. The irregular alternation of two kinds of ion in the lattice corresponds with a temperature independent fluctuation $\overline{\Delta A}$ in the solid, whose value will increase as the electrical difference between the two ions becomes bigger. Such a fluctuation is of course independent of time, *i.e.*, has an infinite relaxation time, but owing to the motion of electricity relative to the lattice it is virtually equivalent to the thermal fluctuations in leading to the degradation of available electrical energy. The temperature law for solid solutions will in this case be written

$$\left(\frac{\partial A}{\partial t}\right)_{\text{unit volume}} = \frac{-K}{\overline{\delta A} + \overline{\Delta A}}\left(\frac{\partial A}{\partial x}\right)^2 = \frac{-K}{kT + \overline{\Delta A}}\left(\frac{\partial A}{\partial x}\right)^2,$$

so that the electrical resistance for solid solutions will be of the form

$$R = 1/\mu = C(T + const),$$

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[1] A. Einstein, *Ann. der Physik*, 1910, 33, 1275

where the temperature independent term increases with increasing difference in the electrical properties of the ions. Many alloys follow this simple law approximately at high temperatures. Transitional metals have an additional resistance owing to the presence of an additional energy fluctuation,[5] and cannot be discussed in terms of this simple theory. Superconductors on the other hand receive a fairly simple thermodynamical interpretation which is discussed in a subsequent paper.

Analogy of the Heat Theorem for Irreversible Processes in the Steady State.

Whenever the statistical fluctuations in a thermodynamic function tend to zero as the temperature of the system tends to zero, an analogy of the Nernst Heat Theorem will apply to irreversible processes. The reason is that the average fluctuations must decrease with temperature, and the relaxation time does not increase as T falls. This is not apparent for the dissipation of available energy in the form written above, according to which $\frac{\partial A}{\partial t}$ appears to become infinite as T tends to zero. This is due to the fact that no restriction has been included on the quantity of electricity passing in unit time, which would also become infinite at 0° K. When such a restriction is included, the analogy of the Heat Theorem would predict

$$\left(\frac{\partial A}{\partial t}\right)_{Q\,=\,\textit{const., unit volume}} \rightarrow 0 \quad \text{as} \quad T \rightarrow 0.$$

This is readily seen to hold for pure metals. For electrical energy

$$\left(\frac{\partial A}{\partial t}\right)_Q = \frac{Q^2}{\mu} \sim Q^2T/b,$$

which tends to zero at absolute zero if the conductivity increases more rapidly than proportional to T. The dissipation of available electrical energy due to the temperature independent " fluctuation " $\overline{\Delta A}$ in solid solutions apparently does not vanish at 0° K.

The Conduction of Heat in Solids.

The conduction of heat in a solid in the steady state, considered from the thermodynamic standpoint, is a case of entropy increase at a rate governed by the fluctuations of entropy of the system. An application of the second law of thermodynamics parallel to that developed for processes involving a decrease in available energy makes it clear that the simplest thermodynamic equation for the increase in entropy per unit volume, owing to the interaction of an entropy gradient with the fluctuations of the system, is

$$\left(\frac{\partial S}{\partial t}\right)_{\text{unit volume}} = K_s\left(\frac{\partial S}{\partial x}\right)^2.$$

If Q is the heat conducted across unit area, and $\frac{\Delta T}{\Delta x}$. dx is the temperature difference across the element of volume considered, then in the steady state the entropy increase in any element of volume will be

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[5] Mott, *Proc. Roy. Soc.*, *A*, 1936, **153**, 699.

$$\frac{1}{\mathrm{d}x}\left(\frac{Q}{T} - \frac{Q}{T+\Delta T}\right) = \frac{Q}{T^2}\,\frac{\mathrm{d}T}{\mathrm{d}x}.$$

Also since

$$\frac{\partial S}{\partial x} = \frac{C_v}{T}\,\frac{\partial T}{\partial x},$$

where C_v has the dimensions of a specific heat, but need not be specified more closely,

$$\left(\frac{\partial S}{\partial t}\right) = K_s\left(\frac{\partial S}{\partial x}\right)^2 = \frac{Q}{T^2}\,\frac{\mathrm{d}T}{\mathrm{d}x} = \frac{K_sC_v^2}{T^2}\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)^2.$$

It will be seen that this is equivalent to the usual equation for the conduction of heat in the steady state

$$Q = K\frac{\mathrm{d}T}{\mathrm{d}x} = K_sC_v^2\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right),$$

where K the thermal conductivity is equal to $K_s \,.\, C_v^2$.

The Wiedemann Franz Law.

The simplest thermodynamic equations for the rate of decrease of available energy and the rate of increase of entropy per unit time are for systems in the steady state,

$$\left(\frac{\partial A}{\partial t}\right)_{\text{unit volume}} = -K_a\left(\frac{\partial A}{\partial x}\right)^2 \quad \text{and} \quad \left(\frac{\partial S}{\partial t}\right)_{\text{unit volume}} = K_s\left(\frac{\partial S}{\partial x}\right)^2.$$

If both equations refer to changes depending upon the same set of fluctuations in a system, the two rates are not independent. Since

$$A = E - TS$$

and the relaxation time of the fluctuations is the same,

$$\left(\frac{\partial A}{\partial t}\right) = T\left(\frac{\partial S}{\partial t}\right),$$

provided the fluctuations in both A and S are independent of T. Using the results already obtained,

$$K_ae^2\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)^2 = T\,.\,\frac{K_sC_v^2}{T^2}\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)^2.$$

or since $K = K_sC_v^2$ and $\mu = K_ae^2$,

$$K/\mu = T\left(\frac{\mathrm{d}V}{\mathrm{d}x}\right)^2\Big/\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)^2.$$

Since the magnitudes of the gradients is a matter of definition of the units, this is equivalent to the Wiedemann Franz law.

This derivation suggests a number of causes leading to a breakdown of the law. This must happen whenever either the value of $\frac{\partial A}{\partial t}$ or $\frac{\partial S}{\partial t}$ fail to obey the simplest equation,[6] or when $\frac{\partial A}{\partial t}$ for example includes a term due to temperature independent "fluctuations."

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[6] Hume Rothery, *The Metallic State*, *Oxford*, 1931, 68.

Other Processes in the Steady State.

A number of other processes can be described making use of the general principle that when the fluctuations in a thermodynamic variable interact with a gradient in the system, they can on the average only lead to an increase in entropy or a decrease in available energy, from the second law of thermodynamics. The simplest physical equations (for small gradients) of a number of irreversible processes thus reduce to the same general form. This may be illustrated with a pair of examples.

Diffusion.

The general equation

$$\left(\frac{\partial A}{\partial t}\right)_{\text{unit volume}} = -K_a\left(\frac{\partial A}{\partial x}\right)^2$$

for the rate of dissipation of available energy applies to the case of diffusion in the steady state, *i.e.*, where the concentration in any layer is kept constant and a concentration gradient is set up. The relation between the available energy and the activity of the solution is

$$A = RT \ln a + \textit{const}, \text{ per mole,}$$

so that the thermodynamic equation transforms to

$$Q \,.\, RT[\Delta \ln a]_{\text{unit volume}} = -K_a \,.\, (RT)^2\left(\frac{\mathrm{d} \ln a}{\mathrm{d}x}\right)^2,$$

where Q is the amount of solute passing through unit volume (*i.e.*, any element of volume) in unit time. This is equivalent to Fick's diffusion law, with the diffusion constant D, since

$$\left(\frac{\partial A}{\partial t}\right)_{\text{unit volume}} = -Q\frac{\partial A}{\partial x} = -K_a\left(\frac{\partial A}{\partial x}\right)^2,$$

$$Q = -K_a\left(\frac{\partial A}{\partial x}\right) = \frac{K_a \,.\, RT}{a}\,\frac{\mathrm{d}a}{\mathrm{d}x}.$$

It is to be noted that this equation differs from Fick's diffusion law in the steady state by the occurrence of thermodynamic activities, a, in place of concentrations. Most experiments are conducted on solutions so dilute that this point cannot be tested. The diffusion constant

$$D = K_a \,.\, RT/a.$$

The occurrence of a concentration term in the thermodynamic constant does not necessarily imply that D depends upon concentration, since in the simple derivation of the fundamental equation

$$\left(\frac{\partial A}{\partial t}\right)_{\text{unit volume}} = K_a\left(\frac{\partial A}{\partial x}\right)^2,$$

the magnitude of the fluctuations $[\overline{\delta A}]$ has not been inserted. Where A is a function of the concentration, these fluctuations will likewise depend in magnitude upon the concentration, and the dependence of D on the concentration cannot be decided without a more detailed analysis.

Viscosity.

In this example the rate of dissipation of available energy will in the simplest case depend upon the *square* of the velocity gradient, *i.e.*,

$$\left(\frac{\partial A}{\partial t}\right)_{\text{unit volume}} = -K_a\left(\frac{\partial V}{\partial x}\right)^2.$$

If χ is the force per unit area due to frictional drag, the relative velocity of two layers dx apart is $\frac{dV}{dx}$, and the rate of dissipation of available energy per unit volume will be

$$\frac{\partial A}{\partial t} = \chi\frac{dV}{dx}.$$

The simplest form of viscosity equation thus reduces to Newton's equation

$$\chi\frac{dV}{dx} = K_F\left(\frac{dV}{dx}\right)^2 \quad \text{or} \quad \chi = \eta\frac{dV}{dx},$$

where $\eta = K_F$ is the coefficient of viscosity.

Where the same fluctuations are responsible for thermal conduction, as in a gas, it is again possible to write

$$-T\frac{\partial S}{\partial t} = -\frac{K}{T^2}\left(\frac{\partial T}{\partial x}\right)^2 = \frac{\partial A}{\partial t},$$

so that

$$\eta T = K\left(\frac{\partial T}{\partial x}\right)^2\Big/\left(\frac{\partial V}{\partial x}\right)^2.$$

This relation shows that the viscosity in such a case is proportional to the thermal conductivity, though as in other cases a statistical analysis is required for a complete evaluation of the constants.

Other Irreversible Processes.

The examples selected above for discussion all refer to systems in the steady state, and have been chosen to illustrate what information can be obtained about the velocity of irreversible processes, using the *minimum* of information about the systems concerned. As is the case for systems in equilibrium, a complete statistical treatment gives much more information than a thermodynamic treatment. This does not imply that the thermodynamic treatment is superfluous.

For systems not in a steady state (*e.g.*, a chemical reaction) it still remains true that the maximum velocity of the irreversible change can be correlated with the average fluctuations and their relaxation time in the system. Such a correlation is particularly valuable in cases such as chain reactions or superconducting systems, and is discussed in a forthcoming paper.

Summary.

A method is proposed for correlating the velocity of irreversible processes in a system with the thermodynamic functions of the system. In cases where the kinetic behaviour of the system can be summed up by the average fluctuations in its thermodynamic variables, and their time of relaxation, it is possible to reach conclusions about this kinetic behaviour with far less information about the system than when a complete statistical analysis is attempted. The examples adduced include a derivation of Ohm's law, of the equation for heat conduction, of the Wiedemann Franz law, and of equations for diffusion and viscosity. The velocity of these irreversible processes can thus be correlated with the thermodynamic functions of the system, which normally apply only to equilibrium processes.

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THERMODYNAMICS OF AN ACTIVATED COMPLEX.

By E. A. Guggenheim.

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1. Introduction.—In the highly interesting theory of reaction rates in gases due to Eyring and Polanyi and later generalised by Eyring,[1] the fundamental assumptions concern the nature of the activated complex; we reserve criticism of these assumptions for another paper; if we suppose these assumptions accepted, the rest of Eyring's treatment is an accurate and elegant application of the statistical methods of Darwin and Fowler.[2]

More recently Eyring's model has been extended to reactions in solution,[3] but in these papers the theory has been clothed in quasi-thermodynamic form. Unfortunately the quasi-thermodynamic functions have in many cases been ambiguously defined, and this has led to controversy and confusion.[4] For the purpose of the present paper we will accept the view that one may apply equilibrium theory to the activated complex and shall give as briefly as possible what we believe to be the accurate thermodynamic relations. We shall also point out in what respect they differ from those advanced by other authors. The confusion arises largely but not entirely from the use of standard states introduced by Lewis and Randall,[5] and the lack of sufficient care by subsequent authors in defining their standard states. It is not that the choice of standard state matters very much, but an author who does not trouble to specify his standard states is liable to change them unconsciously.

2. Thermodynamic Definitions of Ideal Systems.—The thermodynamic properties of an ideal system, whether a perfect gas or an ideally dilute solution, may be summarised as follows. If as independent variables are chosen the temperature T, the external pressure P and the mole fractions N_i then the partial molal energies E_i, the partial molal volumes V_i, the partial molal entropies S_i are of the form

$$E_i(T, P, N) = E_i(T, P) \text{ independent of } N_i \quad . \quad . \quad 2.1$$

$$V_i(T, P, N) = V_i(T, P) \text{ independent of } N_i \quad . \quad . \quad 2.2$$

$$S_i(T, P, N) = S_i^0(T, P) - R \log N_i \quad . \quad . \quad . \quad 2.3$$

Consequently the partial molal total heats (or heat contents) H_i and the chemical potentials μ_i are of the form

$$H_i(T, P, N) = H_i(T, P) \text{ independent of } N_i \quad . \quad . \quad 2.4$$

$$\mu_i(T, P, N) = \mu_i^0(T, P) + RT \log N_i \quad . \quad . \quad . \quad 2.5$$

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[1] Eyring and Polanyi, *Z. physikal. Chem. B*, 1931, **12**, 279; Eyring, *J. Chem Physics.*, 1934, **3**, 107.

[2] See Fowler, *Statistical Mechanics*, Cambridge Univ. Press, 1929 or 1936.

[3] Wynne-Jones and Eyring, *J. Chem. Physics.*, 1935, **3**, 492; Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875.

[4] See Moelwyn-Hughes, *ibid.*, 1936, **32**, 1735; Evans and Polanyi, *ibid.*, 1937, **33**, 448.

[5] Lewis and Randall, *Thermodynamics*, McGraw Hill Book Co., 1923.

All these formulæ are familiar but it is unfortunately necessary to emphasise that these simple relations are dependent on our choice of independent variables. If we use different independent variables we cannot express the behaviour of ideal *liquid* systems, by such simple formulæ. (For perfect gases there are alternative formulations almost as simple.) We cannot emphasise too strongly that T, P, N_i are independent variables throughout; having made this clear, we shall for the sake of brevity usually omit to designate the independent variables explicitly.

Remembering what are the independent variables, we have

$$T^2 \frac{\partial \mu_i/T}{\partial T} = -H_i \quad . \quad . \quad . \quad . \quad . \quad 2.6$$

$$\frac{\partial \mu_i}{\partial P} = V_i \quad . \quad . \quad . \quad . \quad . \quad . \quad 2.7$$

3. Homogeneous Equilibria in Ideal Systems.—The thermodynamic equilibrium condition for the process

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{X} \quad . \quad . \quad . \quad . \quad . \quad 3.1$$

is

$$\mu_{\mathrm{A}} + \mu_{\mathrm{B}} = \mu_{\mathrm{X}} \quad . \quad . \quad . \quad . \quad . \quad 3.2$$

For an ideal system, whether perfect gas or ideal dilute solution, this leads to

$$\frac{N_{\mathrm{X}}}{N_{\mathrm{A}} N_{\mathrm{B}}} = K(T, P) \quad . \quad . \quad . \quad . \quad . \quad 3.3$$

where

$$\begin{aligned} RT \log K &= \mu_{\mathrm{A}}{}^0 + \mu_{\mathrm{B}}{}^0 - \mu_{\mathrm{X}}{}^0 \\ &= (H_{\mathrm{A}} + H_{\mathrm{B}} - H_{\mathrm{X}}) - T(S_{\mathrm{A}}{}^0 + S_{\mathrm{B}}{}^0 - S_{\mathrm{X}}{}^0) \\ &= (E_{\mathrm{A}} + E_{\mathrm{B}} - E_{\mathrm{X}}) + P(V_{\mathrm{A}} + V_{\mathrm{B}} - V_{\mathrm{X}}) \\ &\qquad - T(S_{\mathrm{A}}{}^0 + S_{\mathrm{B}}{}^0 - S_{\mathrm{X}}{}^0) \quad . \quad . \quad 3.4 \end{aligned}$$

Remembering what are the independent variables we have

$$RT^2 \frac{\partial \log K}{\partial T} = H_{\mathrm{X}} - H_{\mathrm{A}} - H_{\mathrm{B}} = \Delta H \quad . \quad . \quad 3.5$$

$$RT \frac{\partial \log K}{\partial P} = V_{\mathrm{A}} + V_{\mathrm{B}} - V_{\mathrm{X}} = -\Delta V \quad . \quad . \quad 3.6$$

where the operator Δ refers to the excess of a value for X over the sum of the values for A and B. We also have

$$\frac{\partial \Delta H}{\partial T} = \Delta C_{\mathrm{P}} \quad . \quad . \quad . \quad . \quad . \quad 3.7$$

where C_{P} denotes the molal heat capacity at constant pressure and

$$\frac{\partial \Delta H}{\partial P} = \Delta V - T \frac{\partial \Delta V}{\partial T} . \quad . \quad . \quad . \quad . \quad . \quad 3.8$$

4. Transformation of Formulæ for Gases and for Extremely Dilute Solutions.—It is usual in practice, presumably from habit, to work in terms of concentrations instead of mole-fractions. We shall accordingly transform our formulæ. It is important to notice that the transformation is quite different for gases and liquids.

For gases we have

$$C_i = N_i \frac{P}{RT} . \quad . \quad . \quad . \quad . \quad . \quad 4.1$$

This leads to

$$S_i = S_i^{0\prime} - R \log C_i \quad . \quad . \quad . \quad 4.21$$

$$\mu_i = \mu_i^{0\prime}(T) + RT \log C_i \quad . \quad . \quad 4.22$$

$$\mu_i^{0\prime} = E_i + RT - TS_i^{0\prime}, \quad . \quad . \quad . \quad 4.23$$

$$\frac{C_X}{C_A C_B} = K_c(T) \text{ independent of } P, \quad . \quad . \quad 4.31$$

$$RT \log K_c = \mu_A^{0\prime} + \mu_B^{0\prime} - \mu_X^{0\prime}, \quad . \quad . \quad . \quad 4.32$$

$$RT^2 \frac{\partial \log K_c}{\partial T} = E_X - E_A - E_B = \Delta E. \quad . \quad . \quad 4.33$$

These formulæ are so familiar as to require no further discussion. They are included merely for contrast with the corresponding formulæ for liquid solutions.

To transform our formulæ for liquid solutions we shall suppose these to be "extremely dilute."[6] We then have for each solute species s the approximation

$$\begin{aligned} C_s &= \frac{N_s}{N_l V_l + \sum_s N_s V_s} \\ &\sim \frac{N_s}{N_l V_l + \sum_s N_s V_l} \\ &= \frac{N_s}{V_l} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 4.4 \end{aligned}$$

where the subscript l refers to the solvent. Using this substitution we obtain

$$S_i = S_i^{0\prime}(T, P) - R \log C_i ; \; S_i^{0\prime} = S_i^0 - R \log V_l \, . \quad 4.51$$

$$\mu_i = \mu_i^{0\prime}(T, P) + RT \log C_i ; \; \mu_i^{0\prime} = \mu_i^0 + RT \log V_l \quad 4.52$$

$$\frac{C_X}{C_A C_B} = K_c ; \; K_c = K V_l \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad 4.6$$

$$RT \log K_c = \mu_A^{0\prime} + \mu_B^{0\prime} - \mu_X^{0\prime} \quad . \quad . \quad . \quad . \quad . \quad 4.7$$

$$RT^2 \frac{\partial \log K_c}{\partial T} = H_X - H_A - H_B + RT \frac{\partial \log V_l}{\partial T} = \Delta H + RT^2 \alpha_l \quad 4.8$$

$$\begin{aligned} RT \frac{\partial \log K_c}{\partial P} &= V_A + V_B - V_X + RT \frac{\partial \log V_l}{\partial P} \\ &= -\Delta V - RT\beta_l \quad . \quad . \quad . \quad . \quad . \quad . \quad 4.9 \end{aligned}$$

where α_l denotes the coefficient of thermal expansion and β_l the compressibility of the solvent. The occurrence of terms of the type of those involving α_l, β_l has been pointed out in a different correction by Bell and Gatty.[7]

In all these formulæ V_A is, of course, the molar volume of A, not the volume of solution containing a mole of A as stated by Evans and Polanyi. The same remark applies to V_B, V_X, V_s, V_l.

5. Application to Activated Complex.—If for the moment we accept the view that the activated complex is in equilibrium with the reactants, then we can make X denote the activated complex and all the previous formulæ are valid. It is, however, necessary to be precise in the definition of the activated complex. On Eyring's theory this is defined as a pair of molecules A, B such that a certain co-ordinate, called the reaction co-ordinate, has a value lying in a specified elementary range of arbitrary length δ, while all the other co-ordinates of the molecule pair may have any value consistent with this. Thus the equilibrium number of activated complexes will be proportional to the length arbitrarily assigned to δ, provided δ is sufficiently small. On Eyring's theory the rate of reaction is directly proportional to the equilibrium number of activated complexes and inversely proportional to their mean life. But the mean life of an activated complex is equal to δ divided by the mean velocity corresponding to the reaction co-ordinate. Thus in the final value for the reaction rate, the length δ cancels, as it obviously must.

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[6] For definition, see Guggenheim, *Modern Thermodynamics*, Methuen, 1933.

[7] Bell and Gatty, *Phil. Mag.*, 1935, **19**, 75.

In order to obtain thermodynamic functions independent of the arbitrary length δ, one may adopt one of two alternatives. Evans and Polanyi define an "equilibrium factor" **K** by

$$K_c = \mathbf{K}\delta \qquad . \quad . \quad . \quad . \quad . \quad 5.1$$

or

$$\mathbf{K} = \frac{\mathbf{C_X}}{C_A C_B} \qquad . \quad . \quad . \quad . \quad . \quad 5.2$$

where $\mathbf{C_X}$ denotes the number of activated complexes per unit volume of solution and per unit distance along the reaction co-ordinate. Wynne-Jones and Eyring define another "equilibrium factor" (terminology of Evans and Polanyi) $K^{\ddagger}$ by

$$K_c = K^{\ddagger}\frac{(2\pi M_X RT)^{\frac{1}{2}}\delta}{h} \qquad . \quad . \quad . \quad 5.3$$

or

$$K^{\ddagger} = \frac{C_X^{\ddagger}}{C_A C_B} \qquad . \quad . \quad . \quad . \quad . \quad . \quad 5.4$$

where M_X is the reduced molar mass (chemical molecular weight) and h is Planck's constant. $C_X^{\ddagger}$ denotes the number of activated complexes per unit volume of solution and per area h in the phase plane of the reaction co-ordinate and its conjugate momentum. Either **K** or $K^{\ddagger}$ is equally utilisable provided they be not confused.

Assuming that the reactant A is not also a product of the reaction (*i.e.* that A is not a catalyst), the velocity constant k is defined by

$$-\frac{\partial C_A}{\partial t} = kC_A C_B \qquad . \quad . \quad . \quad . \quad 5.5$$

where $\partial C_A/\partial t$ denotes the rate of the forward reaction. Then on Eyring's theory k is given by

$$k = \left(\frac{RT}{2\pi M_X}\right)^{\frac{1}{2}}\mathbf{K}$$

$$= \frac{RT}{h}K^{\ddagger} \qquad . \quad . \quad . \quad . \quad . \quad 5.6$$

the factor before **K** being a linear velocity, that before $K^{\ddagger}$ a frequency. Moelwyn Hughes[8] confuses these two factors with different dimensions.

6. Activation Energy.—If we accept the same convention as Eyring the activation energy ϵ is defined by

$$\epsilon = RT^2\frac{\partial \log k}{\partial T} - \tfrac{1}{2}RT. \quad . \quad . \quad . \qquad 6.1$$

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[8] *Loc. cit.*,[4] p. 1730 near top.

By comparison with (5.6) we see that

$$\epsilon = RT^2\frac{\partial \log \mathbf{K}}{\partial T}$$

$$= RT^2\frac{\partial \log K^{\ddagger}}{\partial T} + \tfrac{1}{2}RT \quad . \quad . \quad . \quad 6.2$$

For gaseous reactions we have by comparison of (5.6) and (4.33)

$$RT^2\frac{\partial \log \mathbf{K}}{\partial T} = \Delta E, \quad . \quad . \quad . \quad . \quad . \quad 6.3$$

$$RT^2\frac{\partial \log K^{\ddagger}}{\partial T} = \Delta E - \tfrac{1}{2}RT. \quad . \quad . \quad . \quad 6.4$$

Evans and Polanyi [9] make the cryptic suggestion that only **K** and not $K^{\ddagger}$ may be regarded as a thermodynamic variable, but they do not define their conception of a thermodynamic variable. They do, however, mention as grounds for their preference for **K** over $K^{\ddagger}$, that they "can see no physical meaning" in the expression $\Delta E - \frac{1}{2}RT$ occurring on the right of (6.4). It should be obvious that this quantity is the excess energy of X over A and B, omitting the kinetic energy associated with the reaction co-ordinate. Adopting the same definition (6.1) of "activation energy" for reactions in extremely dilute ideal solutions, we obtain from (5.6) and (4.8)

$$\epsilon = RT^2\frac{\partial \log \mathbf{K}}{T}$$

$$= \Delta H + RT^2\alpha_l. \quad . \quad . \quad . \quad . \quad . \quad 6.5$$

7. Dependence of Activation Energy on Pressure.—To obtain the dependence of the activation energy on the pressure, we have to differentiate (6.5) with respect to P. We obtain

$$\frac{\partial \epsilon}{\partial P} = \Delta V + T\frac{\partial \Delta V}{\partial T} + RT^2\frac{\partial \alpha_l}{\partial P}. \quad . \quad . \quad 7.1$$

If we may neglect compressibility, so that ΔV is independent of P and α_l is independent of P, but do not neglect thermal expansion, we can integrate (7.1) and obtain

$$\epsilon(T, P) = \epsilon(T, 0) + P\left\{\Delta V - T\frac{\partial \Delta V}{\partial T}\right\} \quad . \quad . \quad . \quad 7.2$$

in agreement with Evans and Polanyi (apart from a trivial error of sign), who however omit to state that compressibility is neglected. We agree with these authors that a different formula, given by Moelwyn Hughes and misquoted by Evans and Polanyi, is wrong, but not for the reason given by the latter. They say: "To obtain E_A (our ϵ) we have to differentiate at constant pressure since the measured values of E_A at ordinary pressures as well as under hydrostatic pressures *are all referred to constant pressure.*" The words which we have put in italics seem to us devoid of any meaning. The correct reason for keeping the pressure constant, as explained in section 2, is that temperature, pressure and mole fractions, are the independent variables in the simple formulæ by which ideal systems have been defined and therefore also in all formulæ derived from these. Moelwyn Hughes' differentiation of his formula (52) leading to his (55) is meaningless; he appears to be trying to vary T keeping both P and V constant.

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[9] Evans and Polanyi, *Trans Faraday Soc.*, 1937, **33**, 449.

8. Standard Entropy Differences.—Let us now return to the general thermodynamic relations of the first four sections, forgetting for the moment that X is to be an activated complex rather than a normal molecular species. Now consider the process

$$\mathrm{A}(N_{\mathrm{A}} = N_{\mathrm{A}}{}^{0}) + \mathrm{B}(N_{\mathrm{B}} = N_{\mathrm{B}}{}^{0}) \rightarrow \mathrm{X}(N_{\mathrm{X}} = N_{\mathrm{X}}{}^{0}) \quad . \quad 8.1$$

then

$$\Delta S = S_{\mathrm{X}}{}^{0} - S_{\mathrm{A}}{}^{0} - S_{\mathrm{B}}{}^{0} - R \log \frac{N_{\mathrm{X}}{}^{0}}{N_{\mathrm{A}}{}^{0} N_{\mathrm{B}}{}^{0}} \quad . \quad . \quad 8.2$$

If we so choose $N_{\mathrm{A}}{}^{0}$, $N_{\mathrm{B}}{}^{0}$, $N_{\mathrm{X}}{}^{0}$ that $N_{\mathrm{X}}{}^{0}/N_{\mathrm{A}}{}^{0}\, N_{\mathrm{B}}{}^{0}$ is unity we obtain

$$\Delta S = S_{\mathrm{X}}{}^{0} - S_{\mathrm{A}}{}^{0} - S_{\mathrm{B}}{}^{0} = \Delta S^{0} \quad . \quad . \quad 8.3$$

This quantity, if any, *ought* to be called the *standard entropy* change for the process

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{X}$$

It has exactly the dimensions of an entropy, being measureable for instance in calories /°C. (The growing practice of saying that an entropy difference is equal to so many " entropy units " is about as illuminating as the statement that a pressure is equal to so many pressure units.)

Now consider the slightly different process

$$\mathrm{A}(C_{\mathrm{A}} = C_{\mathrm{A}}{}^{0}) + \mathrm{B}(C_{\mathrm{B}} = C_{\mathrm{B}}{}^{0}) \rightarrow \mathrm{X}(C_{\mathrm{X}} = C_{\mathrm{X}}{}^{0}) \quad . \quad . \quad 8.4$$

and choose $C_{\mathrm{A}}{}^{0}$, $C_{\mathrm{B}}{}^{0}$, $C_{\mathrm{X}}{}^{0}$ such that $C_{\mathrm{X}}{}^{0}/C_{\mathrm{A}}{}^{0}\, C_{\mathrm{B}}{}^{0}$ is unity. We then obtain for this process

$$\Delta S = S_{\mathrm{X}}{}^{0\prime} - S_{\mathrm{A}}{}^{0\prime} - S_{\mathrm{B}}{}^{0\prime} = \Delta S^{0\prime} \quad . \quad . \quad . \quad 8.5$$

This is the kind of quantity often called the standard entropy change for the process

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{X}$$

It is, however, important to realise that the statement that $\Delta S^{0\prime}$ is equal to so many calories /°C is meaningless unless it stated what is the unit of volume. The dimensions of $\Delta S^{0\prime}$ can be described as :—

$$\{\text{pure number} + \log\,(\text{volume})\} \times \text{entropy}$$

and in no simpler way. Other authors have made confusion worse confounded by omitting the word " standard " and writing of the entropy change of the reaction. Exactly analogous remarks apply to the standard Gibbs free energy G^{0}. The relation

$$\Delta G^{0} = - RT \log K \quad . \quad . \quad . \quad . \quad 8.6$$

where K is defined by (3.3) is unobjectionable, but the common relation

$$\Delta G^{0\prime} = - RT \log K_{c} \quad . \quad . \quad . \quad . \quad 8.7$$

equates two quantities each of the dimensions

$$\{\text{pure number} + \log\,(\text{volume})\} \times \text{energy}$$

The omission of the superscripts as in

$$\Delta G = - RT \log K_{c} \quad . \quad . \quad . \quad . \quad 8.8$$

is particularly objectionable.

We would again emphasise that whereas for a process occurring between a specified initial pressure P_1 and a specified final pressure P_2, *not necessarily equal to each other,*

$$T^2\left(\frac{\partial \Delta G^0/T}{\partial T}\right)_{P_1, P_2} = -\Delta H, \qquad 8.91$$

on the other hand

$$T^2\left(\frac{\partial \Delta G^{0\prime}/T}{\partial T}\right)_{P_1, P_2} \neq -\Delta H. \qquad 8.92$$

The correct equality is for a reaction between perfect gases

$$T^2\left(\frac{\partial \Delta G^{0\prime}/T}{\partial T}\right)_{P_1, P_2} = -\Delta E, \qquad 8.93$$

and for a reaction in an extremely dilute ideal solution, neglecting compressibility,

$$T^2\left(\frac{\partial \Delta G^{0\prime}/T}{\partial T}\right)_{P_1, P_2} = -(\Delta H - \Delta n R T^2 \alpha_l), \qquad 8.94$$

where Δn is the increase in the number of molecules in the chemical process and α_l is the coefficient of thermal expansion of the solvent.

Furthermore, for a reaction taking place at a constant pressure P, whereas

$$\frac{\partial \Delta G^0}{\partial P} = \Delta V, \qquad 8.95$$

$$\frac{\partial \Delta G^{0\prime}}{\partial P} \neq \Delta V. \qquad 8.96$$

The correct equality is for a reaction between perfect gases

$$\frac{\partial \Delta G^{0\prime}}{\partial P} = 0, \qquad 8.97$$

and for a reaction in an extremely dilute ideal compressible solution

$$\frac{\partial \Delta G^{0\prime}}{\partial P} = \Delta V - \Delta n R T \beta. \qquad 8.98$$

This shows the danger of assuming relations between ΔE, ΔH, $\Delta S^{0\prime}$ to be of the same form as the well-known relations between ΔE, ΔH, ΔS^0.

The striking difference between the formulæ for liquids and those for gases is due to the differences in compressibility. For liquids we assume the compressibility independent of pressure while for gases we have the compressibility inversely proportional to the pressure.

9. Entropy of Activation.—Seeing the confusion that can arise from the use of standard entropy differences for processes involving only well-defined molecules, it is hardly surprising that confusion has in fact arisen over the expression "entropy of activation." There are, at least, two expressions that qualify equally well, or rather equally badly, for this name.

When X denotes a normal molecule we have

$$RT \log K_c = (E_A + E_B - E_X) + P(V_A + V_B - V_X) - T(S_A^{0\prime} + S_B^{0\prime} - S_X^{0\prime}) \qquad 9.1$$

Analogously we can define $\mathbf{S}_X$, $S_X^{\ddagger}$ in terms of $\mathbf{K}$, $K^{\ddagger}$ respectively by

$$RT \log \mathbf{K} = (E_A + E_B - E_X) + P(V_A + V_B - V_X) - T(S_A^{0'} + S_B^{0'} - \mathbf{S}_X) \quad . \quad 9.2$$

$$RT \log K^{\ddagger} = (E_A + E_B - E_X) + P(V_A + V_B - V_X) - T(S_A^{0'} + S_B^{0'} - S_X^{\ddagger}) \quad . \quad 9.3$$

Both $(\mathbf{S}_X - S_A^{0'} - S_B^{0'})$ and $(S_X^{\ddagger} - S_A^{0'} - S_B^{0'})$ have unfortunately been called the entropy of activation. Pursuing the analogy one might define $\Delta\mathbf{G}$, $\Delta G^{\ddagger}$ by

$$\Delta\mathbf{G} = -RT \log \mathbf{K} \quad . \quad . \quad . \quad . \quad 9.4$$

$$\Delta G^{\ddagger} = -RT \log K^{\ddagger} \quad . \quad . \quad . \quad . \quad 9.5$$

and pursuing the same unfortunate nomenclature either of these would be called the Gibbs free energy of activation.

The terminology of the whole subject is so confusing and objectionable, that the only safe procedure is to define one's symbols explicitly and use them consistently. As a last example of the prevailing confusion, we would draw attention to the fact that in liquid solutions the so-called energy of activation is according to the formulæ of section 4, in fact a "total heat of activation"

10. Conclusion. This note is preliminary to a paper to be published with Dr. Weiss discussing the fundamental assumptions of Eyring's theory, which for the purposes of the present paper have been accepted.

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THE PRIMARY PROCESS OF PHOTODISSOCIATION IN SULPHUR TRIOXIDE.

By G. Kornfeld.

Received 30th November, 1936.

When, to obtain its absorption spectrum, sulphur trioxide is illuminated with the ultraviolet light of a hydrogen discharge, the very strong absorption bands of sulphur dioxide are always obtained if the trioxide is kept stationary instead of in rapid flow in the absorption tube. This fact, observed by Kornfeld and Weegmann,[1] and recently confirmed by Fajans and Goodeve,[2] indicates that the photo-dissociation of SO_3 could easily be detected by means of the SO_2 absorption bands. In the present investigation these bands were used to determine the spectral range of photo-dissociation in SO_3 and, accordingly, the energy required for that process. Fajans and Goodeve have shown that (according to Coehn and Becker,[3] who used ultraviolet light transmitted through "Uviolglass") SO_3 should be decomposed by ultraviolet light on the long wave-length side of 2500 Å.

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[1] G. Kornfeld and E. Weegmann, *Z. Elektroch.*, 1930, **36**, 789.

[2] E. Fajans and C. F. Goodeve, *Trans. Faraday Soc.*, 1936, **32**, 511.

[3] A. Coehn, *Z. Elektroch*, 1907, **13**, 545.

These authors' results, however, are not quite conclusive, since the "Uviolglass" they used was extraordinarily transparent for shorter wave-lengths.[1] On the other hand, the continuous absorption of SO_3 in the region $\lambda > 2700$ Å. found by Fajans and Goodeve favours the argument that SO_3 dissociation is caused by light of these longer wave-lengths. It seemed advisable, anyhow, to establish definitely the spectral region of photo-decomposition in SO_3.

Experimental.

Pure SO_3 (Kahlbaum) was twice fractionated, a quartz absorption tube filled with the middle fraction and then sealed off. Since it was essential to eliminate SO_2 as far as possible, the following precautions were taken: quartz and glass were connected by sealed joints, and "*Zerschlageventile*" were used instead of taps; before any connection was sealed off, the SO_3 in the apparatus was condensed with liquid air to prevent decomposition by the heat of the flame, and the crystallised SO_3 was shielded against the light of the flame.

The quartz absorption tube, 40 cm. long, laterally connected with a small tube kept at about 11° C. during the illumination, was adjusted before the slit of a Hilger Quartz Spectrograph E 316 (dispersion about 10 A. per millimetre at 2700 Å.), and illuminated from a hydrogen discharge, the light of which was filtered at first through 10 cm. of a 0·0025 *N* solution of barbituric acid in water, and, later, through 10 cm. of a 0·01 *N* solution of potassium iodide. Both filters showed complete absorption in the short wave-length region, with the absorption falling off rather suddenly towards longer wave-lengths. This was found to occur at 2760 Å. with barbituric acid, and at 2650 Å. with the potassium iodide filter.

Results.

Very faint absorption bands of SO_2 were visible on the plate after only eight minutes' exposure with ultraviolet light up to 2760 A., which increased during a second exposure of sixteen minutes, the bands extending towards longer wave-lengths. After the first exposure the weak bands side could only be traced to 3070° Å., whereas the limit was found to be at 3100 Å. after the second exposure. Again, after a sixteen minutes' exposure with ultraviolet light up to 2650 Å. the long wave-length limit of the bands had moved to 3110 A. and, after an hour's irradiation with the same light, a further sixteen minutes' exposure showed the limit to be at 3130 Å.

Discussion.

Since irradiation with light of wave-lengths longer than 2760 Å. causes the decomposition of sulphur trioxide, we now seek to explain the process.

By spectroscopic investigations the energy of dissociation for O_2 is known[4] to be 5·09 V. or 117·3 Cal., for SO it has been found[5] to be 5·05 V. or 116·5 Cal. From thermochemical measurements Bonhoeffer and Harteck[6] have calculated the energies corresponding to the formation of SO_2 and SO_3 from their atomic components. The following four equations are obtained:

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[4] K. F. Bonhoeffer and P. Harteck, *Grundlagen d. Photoch.*, 1933, p. 79.
[5] E. V. Martin, *Physic. Rev.*, 1932, 41, 167.
[6] K. F. Bonhoeffer and P. Harteck, *loc. cit.*, p. 80.

$$O + O = O_2 + 117{\cdot}3 \text{ Cal.} \tag{1}$$
$$S + O = SO + 116{\cdot}5 \text{ Cal.} \tag{2}$$
$$S + 2O = SO_2 + 252{\cdot}6 \text{ Cal.} \tag{3}$$
$$S + 3O = SO_3 + 343{\cdot}0 \text{ Cal.} \tag{4}$$

These equations, together with the value of 45 Cal. for the transition $^3P \rightarrow {}^1D$ of O give the energies for three different processes of dissociation :

$$SO_3 = SO_2 + O - 90{\cdot}4 \text{ Cal.} \tag{5}$$
$$SO_3 = SO + O_2 - 109{\cdot}2 \text{ Cal.} \tag{6}$$
$$SO_3 = SO_2 + O\,^1D - 135{\cdot}4 \text{ Cal.} \tag{7}$$

Since the radiation corresponding to 109·2 Cal. has a wave-length of 2600 Å. there could not have been, in the present investigation, any decomposition of SO_3 into SO and O_2, so that equation (5) describes the only process for which the energy used in these experiments would be sufficient, *viz.* 90·4 Cal. corresponding to a wave-length of 3140 Å.

This result seems quite satisfactory, and is in agreement with the primary process assumed by Franck, Sponer and Teller,[7] and by Fajans and Goodeve.[2] It might, however, be objected that the energy values used in equations (3) and (4) are not in complete agreement with the thermochemical data. The energy of combustion of rhombic sulphur to gaseous SO_2 has been found by Eckmann and Rossini [8] to be 70·91 Cal., Kelley [9] has determined the energy required for the evaporation of rhombic sulphur into the diatomic gas to be 30·58 Cal. and the energy of dissociation of S_2 is known by spectroscopical measurements[4] as 102·6 Cal., so that the formation of SO_2 from its atomic components should yield an energy of 254·8 Cal. $(70{\cdot}9 + 30{\cdot}6/2 + 102{\cdot}6/2 + 117{\cdot}3)$. The deviation from the value of 252·6 Cal. in equation (3) is small, but there is a greater deviation in equation (4). Roth, Grau and Meichsner [10] found the value of 23·4 Cal. for the oxidation of gaseous SO_2 to gaseous SO_3 : the heat of reaction with atomic oxygen should accordingly be 82·1 Cal. $(23{\cdot}4 + 117{\cdot}3/2)$, and the energy for the formation of SO_3 from its atomic components 336·9 Cal. $(82{\cdot}1 + 254{\cdot}8)$.* Substituting for equations (3) and (4) the equations

$$S + 2O = SO_2 + 254{\cdot}8 \text{ Cal.} \tag{3a}$$

and

$$S + 3O = SO_3 + 336{\cdot}9 \text{ Cal.} \tag{4a}$$

the resulting values for the primary processes are :

$$SO_3 = SO_2 + O - 82{\cdot}1 \text{ Cal.} \quad . \quad . \quad 3460 \text{ Å.} \tag{5a}$$
$$SO_3 = SO + O_2 - 103{\cdot}4 \text{ Cal.} \quad . \quad . \quad 2750 \text{ Å.} \tag{6a}$$
$$SO_3 = SO_2 + O^1D - 127{\cdot}1 \text{ Cal.} \quad . \quad . \quad 2230 \text{ Å.} \tag{7a}$$

According to these new values, it still appears to be highly improbable that SO_3 is decomposed into SO and O_2, although the possibility cannot be definitely excluded ; but even allowing for a margin of ± 2 Cal. the decomposition by light transmitted through the iodide filter ought to have been of another order than that by light filtered through barbituric acid, if the primary process were to result in SO and O_2 instead of SO_2 and O.

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[7] J. Frank, H. Sponer, and E. Teller, *Z. physik. Chem.*, *B*, 1932, 18, 88.

[8] Landolt-Börnstein, 5. *Aufl. II. Erg. Bd.*, p. 1500.

[9] Landolt-Börnstein, 5 *Aufl. III. Erg. Bd.*, p. 2719.

[10] W. A. Roth, R. Grau, and A. Meichsner, *Z. anorg. Chem.*, 1930, 193, 169.

* There is still some uncertainty, since the dependence on temperature has been neglected for the thermochemical values.

Summary.

By observing the formation of SO_3 absorption bands in SO_2 irradiated with ultraviolet light, the decomposition of SO_3 was found to occur with light of wave-lengths longer than 2760 Å.; this accords with the assumption that the primary process of decomposition results in a SO_2 molecule and an O atom in the normal state.

The author wishes to express her sincere thanks to the American Association of University Women for the International Fellowship of 1935/36 which has enabled her to carry out this investigation. Many thanks are further due to Professor H. Mark, Director of the I. Chem. Institute at the University of Vienna for the hospitality received in his institute; the author feels also indebted to Professor J. Pollak and to Priv. Doz. Ph. Gross, as well as to the Rockfeller Foundation, for having been allowed the use of the spectrograph belonging to the latter institution.

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ABNORMAL VAPOUR PRESSURES IN POTASSIUM CHLORIDE SOLUTIONS.

By H. N. Parton.

Received 1*st March*, 1937.

Studies on the vapour pressure of water in equilibrium with solutions containing potassium and lead chloride have been carried out by Allmand and Hunter[1] and Weir.[2] The former workers, using the method of Pearce and Snow, found abnormally high vapour pressures in a narrow concentration region about the invariant point in the condensed system KCl—$PbCl_2$—H_2O, at which the solid phases are $PbCl_2$ and $2PbCl_2 . KCl$. In the same region Allmand and Burrage[3] have reported anomalous analytical and electromotive force data. Weir extended the work, partly by the Pearce and Snow method and partly by a direct manometric method. He confirmed the previous results.

These studies have now been extended by Weir[4] to solutions of KCl alone, using the Pearce and Snow method, the direct manometric method, and two new methods, one depending on the relative rates of loss of water vapour from a solution and pure water, and the other on the rate of removal of water from a solution by a rapid stream of gas. All methods gave abnormally high vapour pressures of water in equilibrium with solutions containing about 58 grams of KCl per 1000 grams of water.

This paper presents results of further study of these solutions by three methods.

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[1] Allmand and Hunter, *Trans. Faraday Soc.*, 1936, **32**, 502.
[2] Weir, *Collection Czechoslov. Chem. Communications*, 1936, **8**, 93.
[3] Allmand and Burrage, *Trans. Faraday Soc.*, 1933, **29**, 679.
[4] Weir, *Collection Czechoslov. Chem. Communications*, 1936, **8**, 149.

Electromotive Force Measurements.

The activity of KCl in aqueous solutions from 0·2 to 1·2M was determined by measurements of the cell

$$\text{Ag} / \text{AgCl(s)} / \underset{c_1}{\text{KCl}} / \text{K}_x\text{Hg} / \underset{c_2}{\text{KCl}} / \text{AgCl(s)} / \text{Ag}.$$

Actually half-cells were measured and the activities calculated assuming a value for a half-molal solution from other sources.

Experimental.—Potassium amalgam electrodes were made using a 0·2 per cent. amalgam, prepared electrolytically from pure KOH as recommended by Harned.[5] For work in dilute solutions the amalgam is run into the solution in a fine stream. In this work, with relatively strong solutions a slow flowing amalgam as used by MacInnes and Beattie [6] was found easily reproducible with an oxygen-free, flowing solution. While in the double " cell without liquid junction " the potential is independent of the amalgam concentration, this is not so in the half-cells measured. For this reason measurements on the 0·5M solution were repeated at frequent intervals, and no variation in the E.M.F. found.

Silver-silver chloride electrodes were of the type used by Brasher and Parton.[7] KCl was purified by being thrown down from solution by gaseous HCl, dried and heated strongly to remove water. Solutions were prepared with air free water, and stored and manipulated under nitrogen.

The cell was essentially that used by Allmand and Polack,[8] modified to prevent air coming into contact with the solutions. It was in the form of an H, the silver-silver chloride electrode being in one leg in which the solution was stationary. The other leg was modified to permit solution to flow through it, after passing through a thin-walled glass spiral to attain the temperature of the bath. The amalgam which dropped from the nozzle of the potassium electrode collected in an extension of the cell, in such a way that its reaction with the solution did not interfere with the measurements (see Allmand and Polack).

Measurements were made at 25 ± 0·01° C. and were easily reproduced to 0·1 mv.

Results.—Measurements were made in solutions from 0·3M to 1·2M at 0·1M intervals, three determinations in each case. In addition solutions 0·7, 0·737, 0·777, 0·8 and 0·85, which lie about the region of anomalous vapour pressures were measured more often, and in the preparation of these, some samples were made up in the cold, some with heating, and some with A.R. KCl not specially purified. All gave the same value at the given concentration, independent of treatment.

From the measurements, the activities of KCl in the solutions were calculated, assuming the activity coefficient of KCl in a 1M solution to be 0·597 from the data of Harned.[5] From the activities of KCl, that of the water was calculated by the method of Lewis and Randall.[9] If a_1N_1 are the activity and mol. fraction respectively of water, and a_2N_2 refer to KCl, then

$$d \ln \frac{a_1}{N_1} = - \frac{N_2}{N_1} d \ln \frac{a_2}{N_2}.$$

Using common logarithms and integrating

$$\log \frac{a_1}{N_1} - \log \frac{a_1'}{N_1'} = - \int_{N_2'}^{N_2} \frac{N_2}{N_1} d \log \frac{a_2}{N_2}.$$

$\frac{N_2}{N_1}$ for the various solutions was plotted against $\log \frac{a_2}{N_2}$ and from the area under the curve, the difference between the two values of $\log \frac{a_1}{N_1}$ was obtained. A value for a_1 in some solution had to be assumed, and that for the 1M solution was taken as 0·969 from the data of Pearce and Nelson.[10]

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[5] Harned, *J.A.C.S.*, 1925, 47, 676.

[6] MacInnes and Beattie, *ibid.*, 1920, 42, 1117.

[7] Brasher and Parton, *Trans. Faraday Soc.*, 1935, 31, 681.

[8] Allmand and Polack, *J.C.S.*, 1919, 115, 1020.

[9] Lewis and Randall, " Thermodynamics," 1923.

From the activity data so obtained, the vapour pressure of water was calculated, assuming $a_1 = \frac{P}{P_0}$ where $P_0 = 23{\cdot}752$, the vapour pressure of H_2O in mm. Hg. at 25° C and P = vapour pressure of H_2O in equilibrium with a KCl solution.

The data used are given in Table I.

TABLE I.

m.	a_2.	$\frac{N_2}{N_1}$.	log $\frac{a_2}{N_2}$.	a_1.	P.
0·300	0·0417	0·0054	0·8597	0·992	23·56
0·400	0·0686	0·0072	0·9817	0·988	23·46
0·500	0·1018	0·0090	1·0570	0·985	23·39
0·600	0·1416	0·0108	1·1219	0·982	23·32
0·700	0·1896	0·0126	1·1826	0·978	23·24
0·737	0·2068	0·0133	1·1982	0·977	23·21
0·777	0·2283	0·0140	1·2185	0·976	23·18
0·800	0·2406	0·0144	1·2288	0·975	23·17
0·850	0·2662	0·0153	1·2464	0·974	23·13
0·900	0·2944	0·0162	1·2664	0·972	23·09
1·000	0·3565	0·0180	1·3042	0·969	23·02
1·200	0·4961	0·0216	1·3701	0·963	22·87

In Table II. the values for the aqueous vapour pressure in equilibrium with KCl solutions obtained in the present work are compared with the values of other workers using different methods. The agreement is satisfactory and no abnormal values have been obtained.

TABLE II.

m.	Hepburn,[11] Dew Point.	Pearce and Snow, Dynamic.	Lovelace, etc.,[12] Static.	E.M.F.
0·25	23·56	23·56	23·57	
0·375	23·46	23·47	23·47	23·49
0·750	23·20	23·19	23·20	23·21
1·000	23·03	23·02	23·01	23·02

Direct Vapour Pressure Method.

The method used was substantially that of Weir, and has been fully described in his paper. Reference will only be made to points in manipulation where changes were made. The main parts of the apparatus were (*a*) a vertical glass tube calibrated by cathetometer readings for use as a burette to deliver known volumes of air free water to (*b*) a bulb immersed in a thermostat at 25 ± 0·01° C. The bulb was connected to (*c*) a mercury manometer housed in a wooden box kept at 28° C. A known weight of KCl was put in the bulb through a narrow neck which was then sealed off. Bulb and manometer were then evacuated with a Hyvac pump. Sufficient water to make the required solution was then forced in from the calibrated tube by raising a mercury reservoir and opening a tap between tube and bulb. When solution had been effected (see below), the manometer levels were taken, giving the vapour pressure of water for the particular solution, and a further quantity of water was added to make a second, more dilute solution, which was

[10] Pearce and Nelson, *J.A.C.S.*, 1932, **54**, 3545.
[11] Hepburn, *Proc. Physic. Soc.*, 1928, **40**, 256.
[12] Lovelace, Frazer and Sease, *J.A.C.S.*, 1921, **43**, 102.

measured as before. The preparation of air free water has been described by Weir.

The main difference in the apparatus as compared with Weir's was the addition of a glass stirrer in the bulb. This contained a small iron core, and by means of a solenoid fitting over the bulb, the stirrer could be moved up and down, and gave rapid mixing of the added water with the previous solution. The greatest difficulty met with was in the addition of further amounts of water after the first solution had been measured. When this was done, the manometer always recorded pressures about 23·76 mm. Hg, the vapour pressure of pure water at 25° C., and it was observed that a small amount of water remained in the side tube connecting the bulb and the measuring tube, on the bulb side of the tap. Naturally the manometer registered the vapour pressure of this, since it was higher than that of the solution. The pressure fell very slowly and it was necessary to speed up the distillation of this quantity of water into the solution, to make the latter its correct strength as determined from the weight of KCl taken, and the weight of water forced over from the calibrated tube. For this purpose the bulb was cooled. Local cooling of the bulb alone with ice water as used by Weir was found unsatisfactory, as the time required to obtain temperature equilibrium again, destroyed the possibility of making several measurements each day. It was finally found necessary to measure one solution each day, the small amount of water being allowed to distil into the solution overnight. To assist this, the water level in the thermostat was lowered so that the side tube was at room temperature, and the thermostat temperature was lowered to 5° C. below room temperature Next morning the thermostat was heated slowly to 25° C. again, and the mano-

TABLE III.

Gms. per 1000 gms. H_2O.	*m.*	*p.*	Gms. per 1000 gms. H_2O.	*m.*	*p.*
1st Run			*2nd Run*		
0·000	0·000	23·77			
0·000	0·000	23·76	77·54	1·04	23·00
135·71	1·820	22·25	70·15	0·919	23·10
91·71	1·230	22·91	61·89	0·830	23·36
79·78	1·070	22·97	59·65	0·800	23·23
66·37	0·890	23·12	55·18	0·740	23·58
64·12	0·860	23·11			to 23·27
58·90	0·790	23·15	55·00	0·738	23·22
57·41	0·770	23·25	50·02	0·671	23·27
52·19	0·700	23·38	47·72	0·640	23·26
49·96	0·670	23·41	41·09	0·551	23·36
43·24	0·580	23·45			
40·26	0·540	23·54			
35·79	0·480	23·36			
3rd Run			*4th Run*		
67·41	0·904	23·11	74·53	1·00	22·99
64·86	0·870	23·11	64·16	0·861	23·13
60·62	0·813	23·15	57·41	0·770	23·21
55·99	0·751	23·23	55·94	0·750	23·22
53·83	0·722	23·24	54·46	0·731	23·24
52·20	0·700	23·25	49·96	0·670	23·26
50·85	0·682	23·25	46·26	0·621	23·29
34·31	0·460	23·42	39·53	0·530	23·38
34·08	0·457	23·42	35·43	0·475	23·40

meter read at half-hour intervals, values constant for three hours being taken for the vapour pressure of the solution.

This manipulation differs from that of Weir, who, lacking a stirrer, mixed his solutions by heating, followed by cooling to condense back any water which had precipitated on the walls of his bulb. Weir claims to have reproduced his values to ± 0·007 mm. Hg. The accuracy obtained in this work is ± 0·015 mm. Hg, as the mean of three readings.

Results.—The results of four runs are given in Table III. The first two figures are values obtained for water after preliminary experiments had established the technique described above. They check well with the value of Pearce and Snow, 23·752 mm. Hg.

1st Run.—The first solution 1·82*M* gave a value below that interpolated from the results of Pearce and Snow (22·36 mm.). The next five values agree fairly well with those of other workers, but at 58 gms. KCl per 1000 gms. of water or 0·78*M*, abnormally high values were obtained down to 40 gms. KCl or 0·54*M*. The solutions which gave high values were observed for two days in each case and nothing was observed which would explain them.

2nd Run.—An abnormal value at 0·83*M* was recorded and at 0·74*M* the heating coil broke and some water precipitated in the connecting tube between bulb and manometer. It was allowed to distil back and an apparently stable pressure of 23·58 mm. Hg was obtained; after cooling overnight the value 23·27 mm. was found, still slightly high (interpolated value 23·22 mm.). This observation may throw some light on abnormal values obtained in this method.

Runs 3 and 4 gave values comparable with those of Pearce and Snow within the limits of accuracy of the method.

Discussion—Only in the 1st series of measurements were abnormal values obtained which could not be explained. Examination of Weir's results with this method suggests that there is one fact common to all series in which high values were obtained, namely that when a solution was made which gave an abnormal result, succeeding solutions were also abnormal with a general tendency to move downwards towards the normal vapour pressure. This suggests lack of equilibrium as the explanation of the results, which is supported by the observations in the second series mentioned above. Weir's own explanation (*loc. cit.*,[4] p. 166) is probably correct, that his method of producing concentration equilibrium by heating and cooling was responsible for the solution attaining a "metastable" state and remaining therein for the short time necessary for a measurement. In this work, after the necessary manipulation had been perfected, it seems that normal values only would be obtained whenever equilibrium has been established.

Thermopile Method.

Hill [13] has described a method of measuring the difference between the vapour pressure of two solutions based on the principle of the wet and dry bulb thermometer. The method has been applied to the study of the KCl solutions with which this work is concerned.

Three thermopiles were supplied by Mr. A. C. Downing of University College, London. Their construction, and the theory of their operation have been discussed by Hill. The instruments have one set of junctions down the middle of one face, and another set down the middle of the opposite parallel face. If one face is covered with a small piece of filter paper wetted with one solution, and the other face with filter paper wetted with a second solution, the different rates of evaporation of the

[13] Hill, *Proc. Roy. Soc., A*, 1930, 127, 9.

two solutions due to their different vapour pressures will set up a temperature difference which will be measured by the current developed in the instrument.

A Zernicke moving coil galvanometer reading at 1 metre to 10^{-9} amps. for 1 mm. deflection was used. The readings double every ten degrees, which is equivalent to an error of 0·007 per cent. in the vapour pressure for 0·001° C. variation in temperature. A large water thermostat was used, gas heated and controlled by a mercury-toluene regulator of large volume. In this bath a Beckmann thermometer showed no movement during a day's run, though it could be read easily to 0·001° C.

TABLE IV.

Gms. KCl per 1000 gms. H_2O.	No. I.		No. II.		No. III	
	Deflection.	V P. Difference.	Deflection.	V P. Difference.	Deflection.	V.P. Difference.
50-54	202	(·035)	200	(·035)	176	(·035)
54-58	79	·014	86	·015	79	·016
58-62	87	·015	76	·013	67	·013

Pieces of filter paper of a size just sufficient to cover the faces of the thermopiles were produced by means of a steel punch, and were hence of uniform size. The area of evaporation was thus the same for each solution. The thermopiles were enclosed in brass cylinders, the walls of which were covered with filter paper saturated with a solution intermediate in concentration between the solutions compared.

This method was used to study solutions between 50 gms. KCl/1000 gms. H_2O (0·66*M*) and 62 gms. KCl/1000 gms. H_2O (0·83*M*). A large number of measurements were made with the combinations 50 against 54, 54-58 and 58-62. The vapour pressure difference for solutions containing 50 and 54 gms. KCl was taken as 0·035 mm. Hg. by interpolation from the values of Pearce and Snow. The values given in Table IV. were calculated from the average deflection given by each thermopile. Then assuming the 50 gm. solution has vapour pressure 23·25 mm. Hg, the figures of Table V. were calculated.

They indicate rather high values for the solutions with 58 and 62 gms. KCl/1000 gms. H_2O.

TABLE V.

Gms. KCl per 1000 gms. H_2O.	V.P. (Thermopile).	V.P. (Pearce & Snow).
50	(23·25)	23·25
54	(23·215)	23·215
58	23·200	23·17
62	23·186	23·13

The primary object of this method was to make a large number of comparisons of the solutions about the "abnormal range," and from that viewpoint it has proved fairly satisfactory. Any really abnormal value of the order found by Weir would have produced a very large deflection and probably lack of steadiness. Nothing of this kind was observed and the deflections were consistent in direction, indicating that the solution of higher concentration always had the lower vapour pressure, while in Weir's work this was not always so. From a more strictly quantitative viewpoint, the method was not made to work really satisfactorily or with the reproducibility obtained by Hill. This may be due partly to a constant, though slight leak to earth which could not be eliminated. A more intensive study of the method than was possible in this work seems necessary to eliminate all sources of uncertainty and establish the conditions for consistent results. The null method used by Hill with a potentiometer might be more satisfactory.

General Discussion.

Of the three methods of a static nature used in this work, the E.M.F. method gave no evidence of abnormality in the activity of KCl which must necessarily accompany any abnormality in the solvent activity of the solutions. Apart from some values in the first, and hence probably the least accurate run, the direct method has also given normal results, and evidence was obtained with regard to the attainment of equilibrium which may help to explain the results of Weir by the same method. The thermopile method, while not brought to a satisfactory conclusion as regards accuracy, also gave no evidence of large abnormalities. It seems probable that solutions of potassium chloride will give vapour pressure lowerings consistent with what is already known about such solutions, when it is certain that equilibrium has been attained between vapour and liquid phases.

No investigation has been made in this work of solutions containing lead chloride, and it is in such solutions that there is considerable evidence of abnormal conditions from several sources. Even leaving aside the results of Weir with the direct static method, there is still the evidence of Hunter and Weir using dynamic methods, and the difficulties encountered by Burrage in solubility and E.M.F. investigations. Till measurements of other properties now in progress are available, theoretical discussion is valueless.

Summary.

1. The activity of potassium chloride has been measured in its aqueous solutions from 0·3*M* to 1·2*M* by means of concentration cells without liquid junction. The vapour pressure of water over the solutions has been calculated from the results.

2. The vapour pressure of water in equilibrium with a number of potassium chloride solutions has been measured by two methods.

3. The results of the above experiments have been compared with previous work on the same solutions.

My thanks are due to Professor A. J. Allmand, under whose direction this work was carried out.

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EQUILIBRIA IN AQUEOUS LEAD CHLORIDE SOLUTIONS.

By L. Wilkinson, N. O. Bathurst and H. N. Parton.

Received 1*st March*, 1937.

The System PbO – HCl – H_2O at 50° and 80° C.

Baxter and Grover[1] have shown that if lead chloride purified by crystallisation from an acid solution and dried by fusion in a current of pure dry hydrogen chloride, is dissolved in water to give an almost saturated solution, an appreciable quantity of basic salt will separate.

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[1] Baxter and Grover, *J.A.C.S.*, 1915, 37, 1027.

They showed also that the fused salt is practically neutral, the basic salt being formed in the process of solution. Some twenty basic lead salts are listed in Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry. Various workers, von Ende,[2] Engel,[3] and Kendall,[4] have shown that with excess HCl, the solid phase in equilibrium with solutions is lead chloride. In the preparation of pure lead chloride for studies in aqueous solutions reported elsewhere, it was found necessary to establish the conditions of equilibrium at temperatures near the boiling-point. These conditions have been studied at 50° C. and 80° C.

Experimental.

Mixtures of the various components, lead chloride and hydrochloric acid in the acid part of the system, and lead oxide with either hydrochloric acid or lead chloride solutions in the basic part, were brought to equilibrium by rotating in sealed tubes in a thermostat at the appropriate temperature 50° C. ± 0·1 or 80° C. ± 0·2. At the higher temperature the framework of the shaker was detachable from the bath, permitting it to be lifted until the tubes lay in the surface, from which they could be easily extracted and clamped in the bath until the solid phase settled. Solid and liquid phases were separated by filtration, using a Gooch crucible with fine holes. Solutions and solid phases were analysed for lead and chloride, the former by precipitation as chromate, and the latter as silver chloride. The solid phases were analysed wet, and their compositions determined graphically by the "residue" method of Schreinemakers.[5] The results were plotted by the graphical method of Jänecke,[6] using rectangular co-ordinates. The equilibrium diagram used is a square of unit side, the corners representing the four compounds in the equilibrium, $\underset{a}{\tfrac{1}{2}\mathrm{PbO}} + \underset{b}{\mathrm{HCl}} \rightleftharpoons \underset{c}{\tfrac{1}{2}\mathrm{PbCl_2}} + \underset{d}{\tfrac{1}{2}\mathrm{H_2O}}$ the number of equivalents being as shown. As these four compounds can be derived from only three independent variables, any phase can be represented by a point whose co-ordinates are $x = \dfrac{b + c}{a + b + c + d}$, $y = \dfrac{a + c}{a + b + c + d}$, in which x and y

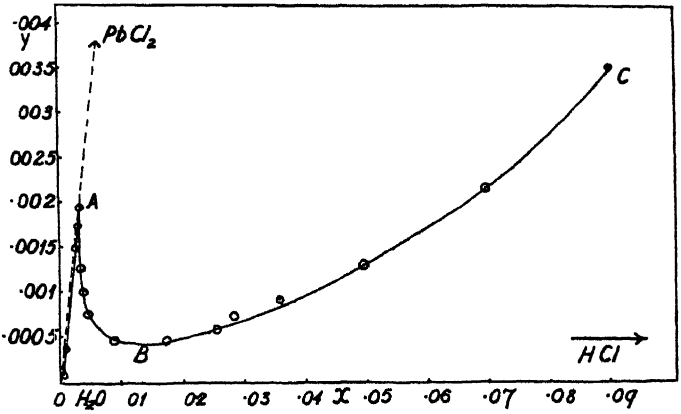

FIG. 1.

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[2] von Ende, *Z. anorg. Chem.*, 1901, **26**, 129.
[3] Engel, *Compt. Rend.*, 1887, **104**, 433.
[4] Kendall, *J.A.C.S.*, 1925, **47**, 2306.
[5] Schreinemakers, *Z. physikal Chem.*, 1893, **11**, 76.
[6] Jänecke, *ibid.*, 1908, **51**, 32; 1911, **71**, 1.

can be calculated from the number of equivalents found by analysis. The origin

$x = y = 0$ represents H_2O.
$x = 0 \quad y = 1$ represents PbO.
$x = 1 \quad y = 0$ represents $PbCl_2 + H_2O - PbO = HCl$
$x = y = 1$ represents $PbCl_2$.

Results.

The values of x and y for solution and wet solid were calculated for each complex from the analysis, and the results plotted as described. A small part only of the graph is reproduced here, sufficient for the main purpose of this investigation. Owing to the low solubility of lead chloride, and its high equivalent weight as compared with that of water, the values of x and y for the solutions are small. In particular the values of y at 50° C. range from 0·0034 to 0·00037. The solution curve is hence scarcely distinguishable from the x axis on the full graph.

At 80° C. it was found possible to differentiate the solution points given by three complexes in which the solid phase, determined by Schreinemaker's method, seemed to be $2PbO, PbCl_2$. This was in equilibrium with solutions from 3 gms. $PbCl_2$ to 24 gms. $PbCl_2$ per thousand gms. of water. This salt has been shown to exist by Ruer[7] from freezing-point determinations on mixtures of PbO and $PbCl_2$. It exists as a mineral mendipite.

TABLE I.

Gms. HCl per 1000 gms. H_2O.	Gms. $PbCl_2$ per 1000 gms. H_2O.	Gms. HCl per 1000 gms. H_2G.	Gms. $PbCl_2$ per 1000 gms. H_2O.
50° C.		**80° C.**	
0·138	16·30	0·563	23·71
0·639	14·35	0·786	23·05
1·317	14·92	2·375	19·50
1·917	11·57	3·479	17·39
3·98	9·24	5·058	15·00
14·20	4·46	10·90	11·49
38·91	3·46	18·90	9·59
45·52	3·25	33·16	7·52
81·86	3·99	67·82	7·57
165·40	7·82	89·45	8·95
184·00	9·27	114·0	11·71
265·00	18·31	147·0	14·24
331·80	27·50	201·2	20·21
377·80	38·16	221·3	22·71
444·4	54·12	286·8	34·77
476·0	61·23	372·5	54·23
		378·1	58·37

At 50° C. the solid phases were identified by drying on a porous plate and analysing. The compounds $3PbO . PbCl_2 . H_2O$ reported by Pleissner[8] were confirmed as stable phases. Pleissner prepared them by shaking the constituents together at 18° C. in the correct molecular proportions. A further compound $4PbO . PbCl_2$, or a hydrate, is formed as a bulky pinkish solid when the components are suspended in water for some hours at 50° C.

Fig. 1 gives the curve at 80° C. on a large scale. The whole of the solution curve lies in the triangle the corners of which represent $PbCl_2$, HCl and H_2O. Hence the solutions are always acid. A similar curve was obtained at 50° C. Solutions along OA are in equilibrium with basic salts, and those represented by ABC with lead chloride. Basic salts can exist in equilibrium with HCl up to about 0·006*M* at 50° C. and 0·02*M* at 80° C. Moreover pure lead chloride dissolved in water must separate into basic salt and solution given by a point on OA. As, however, the line OA almost coincides with that joining O to the opposite corner of the diagram, which represents pure $PbCl_2$ the amount of basic salt produced is very small. It is probable that lead chloride as ordinarily precipitated from acid solution, washed with dilute acid and dried over fused KOH retains the very slight excess of HCl necessary to form a clear solution. The highly purified product, as shown by Baxter and Grover gives a turbid solution.

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[7] Ruer, *Z. anorg. Chem.*, 1906, 49, 365.
[8] Pleissner, *Chem. Zentr.*, 1907, II, 1055.

A. Ditte[8] gave values for the solubility of lead chloride in aqueous hydrochloric acid solutions at various temperatures including 80 C. These results were only available as a table in Seidell's "Solubilities of Inorganic and Organic Compounds," 2nd edition. The HCl concentrations are there expressed as gms. per 1000 gms. H_2O, though the column is headed "per 100 gms. H_2O." The lead chloride concentrations are headed "gms $PbCl_2$ per 100 gms. solution," and again given per 1000 gms.

TABLE II.

Gms. $PbCl_2$ per 1000 gms. H_2O.	Gms. NH_4Cl per 1000 gms. H_2O.	Solid Phase.
10·91	—	$PbCl_2$
3·04	9·62	,,
2·75	13·42	,,
2·15	20·97	,,
2·00	22·34	,,
1·97	26·22	,,
1·76	34·19	,,
1·44	43·03	$PbCl_2 + NH_4Cl . 2PbCl_2$
1·45	44·22	
1·35	48·07	$NH_4Cl . 2PbCl_2$
1·21	65·61	,,
1·22	86·12	,,
1·21	102·1	,,
1·57	146·5	,,
1·97	171·3	,,
3·31	233·5	,,
4·58	270·0	,,
12·27	384·7	,,
13·63	394·5	,,
14·46	403·3	$NH_4Cl . 2PbCl_2 + NH_4Cl$
10·42	403·9	NH_4Cl
7·28	401·1	,,
5·40	400·6	,,
—	397·8	,,

TABLE III.

Gms. $PbBr_2$ per 1000 gms. H_2O.	Gms. NH_4Br per 1000 gms. H_2O.	Solid Phase.
9·81	—	$PbBr_2$
5·72	3·95	,,
2·73	14·44	,,
2·44	20·66	,,
2·00	33·98	$PbBr_2 + NH_4Br . 2PbBr_2$
1·73	42·39	$NH_4Br . 2PbBr_2$
1·55	56·07	,,
1·55	66·88	,,
2·32	135·8	,,
3·92	192·6	,,
13·80	321·3	,,
58·45	500·3	,,
114·90	607·5	,,
118·70	614·4	$NH_4Br . 2PbBr_2 + 2NH_4Br . PbBr_2$
121·70	635·3	$2NH_4Br . PbBr_2$
129·90	699·0	,,
140·7	760·7	,,
148·9	818·7	,,
162·9	886·3	$2NH_4Br . PbBr_2 + NH_4Br$
162·5	889·6	
89·3	843·7	NH_4Br
43·0	825·6	,,
—	793·9	,,

Moreover better agreement with this work is obtained if it is assumed that this should read "gms. per 1000 gms. of H_2O," the assumption being rendered probable since the HCl concentration is expressed in that manner.

Table I. gives the results of this investigation, the experimental work for which was carried out by one of us (L. W.).

The Systems $NH_4Cl - PbCl_2 - H_2O$ and $NH_4Br - PbBr_2 - H_2O$ at 25° C.

A number of investigations on these systems have been carried out and the stability of the double salts $PbCl_2 . 2NH_4Cl$, $2PbCl_2 . NH_4Cl$, $PbBr_2 . 2NH_4Br$, and $2PbBr_2 . NH_4Br$ established.

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[8] Ditte, *Compt. Rend.*, 1881, **92**, 718.

The chloride system has been studied by Foote and Levy[10] at 25° C., Bronsted[11] at 22° C., and Demassieux[12] at 17° C., 50° C. and 100° C. Agreement between the various investigations is not satisfactory, particularly in respect to the position of the transition point between solutions in equilibrium with $PbCl_2$ and those in equilibrium with $NH_4Cl . 2PbCl_2$.

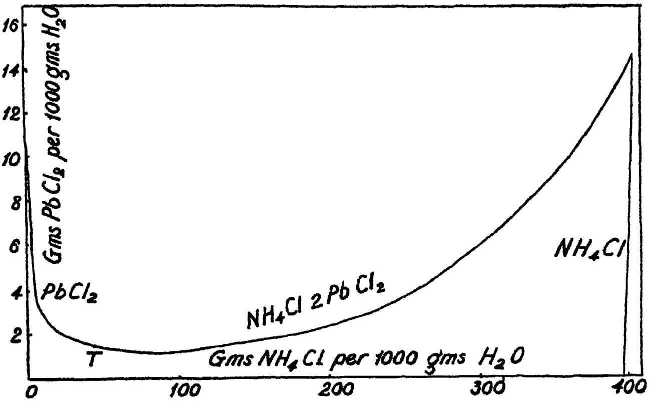

FIG. 2.

The bromide system has been studied by Demassieux and Grelis[13] at 0°, 20° and 50° C. As part of a systematic study of systems of this type at 25° C., measurements are reported here at that temperature.

Preparation of equilibrium mixtures was carried out as in the preceding investigation. The liquid phases were estimated for lead and halide, and the solid phases for lead and ammonia.

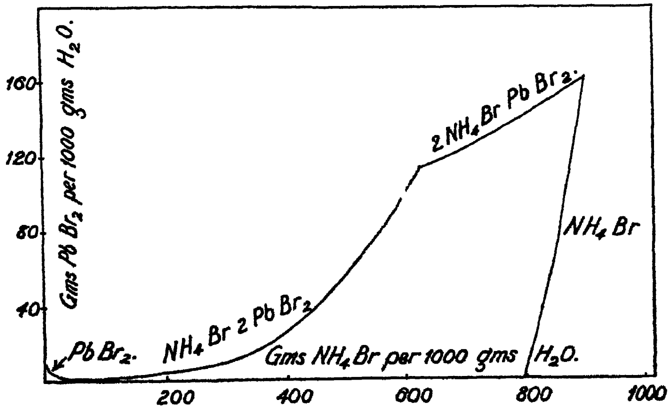

FIG. 3.

Results.

The results are given in Tables II. and III., and represented in Figs. 2 and 3.

[10] Foote and Levy, *Am. Chem. J.*, 1907, **37**, 119.
[11] Brönsted, *7th Intern. Congr. Appl. Chem.*, 1909, Sec. X, 110.
[12] Demassieux, *Compt. Rend.*, 1913, **156**, 894.
[13] Demassieux and Grelis, *ibid.*, 1934, **198**, 179.

Discussion.

The transition point at which the solid phases $PbCl_2$, and $NH_4Cl \cdot 2PbCl_2$ are both stable occurs at a lower NH_4Cl concentration than that which gives the minimum $PbCl_2$ solubility. The point is marked T in Fig. 2. This is in agreement with Brönsted's results at 22° C. Demassieux gave the transition point at the minimum point at the three temperatures studied. Foote and Levy obtained about one-fifth the concentration of lead chloride found in this work at the transition point at 25° C.

In the bromide system the agreement with the results of Demassieux and Grelis at 20° C. is poor. No figures are given in their paper, but as shown in Fig. 4 the shape of the curves at high ammonium bromide concentrations is quite different, as is the shape about the transition point where $PbBr_2$ and $NH_4Br \cdot 2PbBr_2$ co-exist.

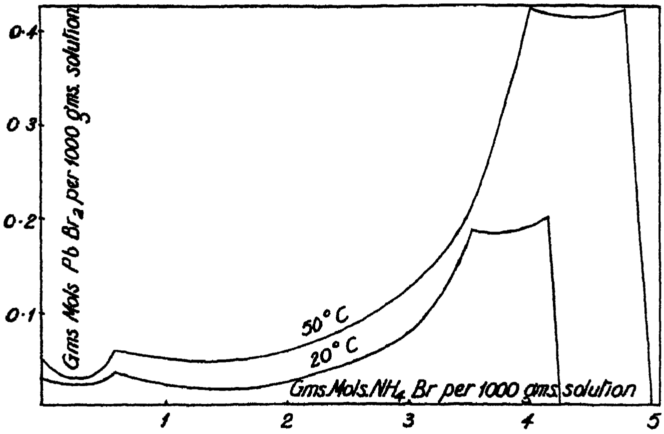

FIG. 4.

The experimental measurements in these systems were made by one of us (N. O. B.).

Summary.

1. The system $PbO—HCl—H_2O$ has been studied at 50° C. and 80° C.
2. Possible basic compounds have been indicated but not definitely established.
3. The conditions of stability of lead chloride in contact with aqueous solutions have been established, and it has been shown that pure lead chloride will hydrolyse in water with separation of a basic salt.
4. The systems $NH_4Cl—PbCl_2—H_2O$ and $NH_4Br—PbBr_2—H_2O$ have been investigated at 25° C. and the results compared with previous work.

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A THERMODYNAMIC STUDY OF SYSTEMS OF THE TYPE $PbCl_2 - RCl - H_2O$ AT 25° C. PART VII.

By E. R. Hounsell and H. N. Parton.

Received 1st *March*, 1937.

Calculations of the activity coefficients of lead chloride in the presence of alkali chlorides from E.M.F. measurements previously reported in this series [1] indicated that in solutions dilute with respect to lead chloride difficulties with dissolved oxygen had caused erroneous results to be obtained. The method used of displacing air by bubbling nitrogen through the cells was found unsatisfactory by one of us (H. N. P.) in very dilute solutions. Measurements now reported have been obtained with a more rigid air-free technique.

Experimental.

The cells were of the type $Pb/PbCl_2 + RCl/AgCl(s)/Ag$. Lead electrodes were of the saturated liquid amalgam type. Silver chloride electrodes were made in batches of eight as previously described (Part III.). Materials were purified as formerly.

The solutions were made up by weight in an atmosphere of pure hydrogen. Distilled water was freed from air by boiling and stored under hydrogen in an apparatus from which it could be delivered in known amounts by means of a compound pipette with three bulbs of 100, 50 and 25 c.c. capacity. Standardised lead chloride and lithium chloride solutions were similarly stored. Potassium and sodium chlorides were weighed out as solids. By hydrogen pressure the required amounts of solution and water were measured into a mixing vessel.

The cell technique was based on that of Cowperthwaite and La Mer.[2] The cells were hermetically sealed with mercury, the air displaced by hydrogen and the lead amalgam run in before the solution was forced in by hydrogen. In this way duplicate cells could be made up which remained constant for at least 12 hours. Measurements were made at 25 ± 0·005° C.

Results.

The complete data are given in Table I. As compared with the results of Allmand and Burrage [1] on the KCl system, the E.M.F.s recorded here are several millivolts lower in the solutions most dilute with respect to lead chloride, the differences being much less in solutions with more than 1 gm. $PbCl_2$ ($0{\cdot}0035M$). In the NaCl system, values about 0·5 mv. lower than those of Brasher and Parton [1] have been obtained for the solutions in which unsteady readings were found by them.

From the E.M.F. readings the activity coefficients of lead chloride in presence of alkali halides have been calculated. La Mer, Gronwall and Greiff [3] give the standard potential of the lead electrode as 0·1269 from the

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[1] Allmand and Burrage, Part II., *Trans. Faraday Soc.*, 1933, **29**, 679; Brasher and Parton, Part III., *ibid.*, 1935, **31**, 681; Parton, Part IV., *ibid.*, 1935, **31**, 685.

[2] Cowperthwaite and La Mer, *J.A.C.S.*, 1931, **53**, 4333.

[3] La Mer, Gronwall and Greiff, *J. Physic. Chem.*, 1931, **35**, 2245.

TABLE I.

$m_1(PbCl_2)$.	$m_2(RCl)$.	E.
$KCl—PbCl_2—H_2O$.		
0·00045	0·0503	0·5417
·00090	,,	·5326
·0018	,,	·5235
·0036	,,	·5140
·0072	,,	·5039
·0108	,,	·4978
0·00045	0·101	0·5328
·00090	,,	·5234
·0018	,,	·5148
·0036	,,	·5052
·0054	,,	·4998
·0072	,,	·4961
0·00045	0·201	0·5252
·00090	,,	·5163
·0018	,,	·5073
·0036	,,	·4983
·0054	,,	·4928
·0072	,,	·4896
0·00045	0·469	0·5197
·00090	,,	·5108
·0018	,,	·5021
·0036	,,	·4934
·0054	,,	·4883
·0072	,,	·4851
0·00045	0·697	0·5296
·0009	,,	·5110
·0018	,,	·5018
·0036	,,	·4930
·0054	,,	·4888
·0072	,,	·4867
$NaCl—PbCl_2—H_2O$.		
0·00045	0·0855	0·5356
·0009	,,	·5263
·0018	,,	·5172
·0036	,,	·5072
·0108	,,	·4919
0·00045	0·171	0·5271
·0009	,,	·5180
·0018	,,	·5089
·0036	,,	·4997
0·00045	0·342	0·5218
·0009	,,	·5123
·0018	,,	·5032
·0036	,,	·4938
$LiCl—PbCl_2—H_2O$.		
0·00045	0·072	0·5377
·0009	,,	·5277
·0018	,,	·5188
·0036	,,	·5091
·0054	,,	·5038
·0072	,,	·4997
·0108	,,	·4938
0·00045	0·144	0·5288
·0009	,,	·5196
·0018	,,	·5103
·0036	,,	·5009
·0054	,,	·4956
·0072	,,	·4918

date of Carmody.[4] Taking the potential of the silver chloride electrode as 0·2221, and the lead-saturated lead amalgam potential as 0·0058, the cell

$$\text{Pb (sat. amalgam)}/\underset{a=1}{\text{Pb Cl}_2}/\underset{(s)}{\text{AgCl}}/\text{Ag}$$

has the value 0·3432.

Then for a cell containing a solution of concentration m_1 of $PbCl_2$ and m_2 of RCl,

$$E = 0{\cdot}3432 - 0{\cdot}08871 \log \gamma \,[m_1(2m_1 + m_2)^2]^{1/3}$$

where γ is the mean activity coefficient of $PbCl_2$ as defined by Lewis and Randall.[5]

This may be transformed into

$$\log \gamma = \frac{0{\cdot}3432}{0{\cdot}08871} - \frac{E}{0{\cdot}08871} - \tfrac{1}{3}\log m_1 - \tfrac{2}{3}\log(2m_1 + m_2).$$

From this formula the activity coefficients given in Table II. have been calculated, using the measurements recorded here and some from Parts III. and IV. of this series.

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[4] Carmody, *J.A.C.S.*, 1929, 51, 2905.

[5] Lewis and Randall, " Thermodynamics," 1923.

TABLE II

RCl m_2 \ $PbCl_2$ m_1	0·00045	0·0009	0·0018.	0·0036.	0·0054	0·0072	0·0108.
(*a*) Activity Coefficients of $PbCl_2$ in KCl Solutions.							
0·0503	0·547	0·544	0·535	0·517	—	0·496	0·473
·101	·437	·440	·432	·430	0·423	·414	
·201	·336	·335	·338	·331	·330	·322	
·469	·221	·221	·219	·217	·215	·212	
·697	·170	·169	·170	·169	·164	·156	
(*b*) Activity Coefficients of $PbCl_2$ in NaCl Solutions.							
0·0855	0·452	0·453	0·449	0·450			0·422
0·171	·356	·357	·356	·354			
0·342	·258	·261	·262	·263			
0·855	·152	·154	·154	·154			
1·711	·089	·089	·089	·090		0·089	
(*c*) Activity Coefficients of $PbCl_2$ in LiCl Solutions.							
0·072	0·479	0·478	0·481	0·476	0·463	0·454	0·439
·144	·381	·383	·381	·382	·378	·373	—
·236	·338	·335	·334	·334	·327	—	—
·472	·252	·252	·252	·250	—	—	—

Discussion.

Similar results have been obtained in all three systems. In Table II.(*a*) it can be seen that at constant $PbCl_2$ concentration, the activity coefficient decreases with increasing KCl concentration. At constant KCl concentration the activity coefficient decreases with increasing $PbCl_2$ concentration in solutions dilute with respect to KCl. At higher KCl concentrations, the activity coefficients tend to become constant independent of the $PbCl_2$ concentration. These general trends are common to all three systems. They are in agreement with the principle of ionic strength of Lewis and Randall,[5] by which "in dilute solutions, the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength." For example in the sodium chloride system, the values fall with increasing $PbCl_2$ for the solutions 0·0855*M* and 0·171*M* with respect to NaCl. This is to be expected as the addition of $PbCl_2$ materially increases the ionic strength. In the stronger solutions of NaCl, however, the fall is very slight, as the $PbCl_2$ makes less and less change in the ionic strength.

Similar results were obtained by Harned[6] for HCl in presence of alkali chlorides. In solutions dilute in HCl, he found that the activity coefficients of the acid are constant at constant total molality. The lead chloride coefficients have been found almost constant in solutions in which the change in total molality is small.

In Fig. 1 the $PbCl_2$ activity coefficients in solutions 0·0036*M* in $PbCl_2$ (1 gm. per 1000 gms. H_2O) have been plotted against ionic strength for the three systems. Some results from Parts III. and IV. of this series are included. In dilute solutions the three curves coincide. In stronger solutions they deviate and at corresponding ionic strengths the activity coefficients of lead chloride are greatest in LiCl solutions and least in KCl solutions. This holds also for other $PbCl_2$ concentrations. The effects are the same as those found by Harned [6] for HCl in alkali chloride solutions and H_2SO_4 in alkali sulphate solutions. He observed

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[6] Harned, *Trans. Faraday Soc.*, 1927, **23**, 462.

that $\gamma_{\mathrm{LiCl}} > \gamma_{\mathrm{NaCl}} > \gamma_{\mathrm{KCl}}$

and that $\gamma_{\mathrm{HCl(LiCl)}} > \gamma_{\mathrm{HCl(NaCl)}} > \gamma_{\mathrm{HCl(KCl)}}$

where $\gamma_{\mathrm{HCl(LiCl)}}$ represents the activity coefficient of HCl in presence of LiCl. From this he deduced

$$\gamma_{\mathrm{H^+(LiCl)}} > \gamma_{\mathrm{H^+(NaCl)}} > \gamma_{\mathrm{H^+(KCl)}}$$

on the assumption of MacInnes [7] that in a chloride solution of given strength and valence type the activity coefficient of the chloride ion is the same, independent of the cation. In the stronger solutions of the systems $PbCl_2$—RCl—H_2O, almost the whole of the chloride ion is contributed by the alkali chloride, and the same assumption may be made. It then follows that

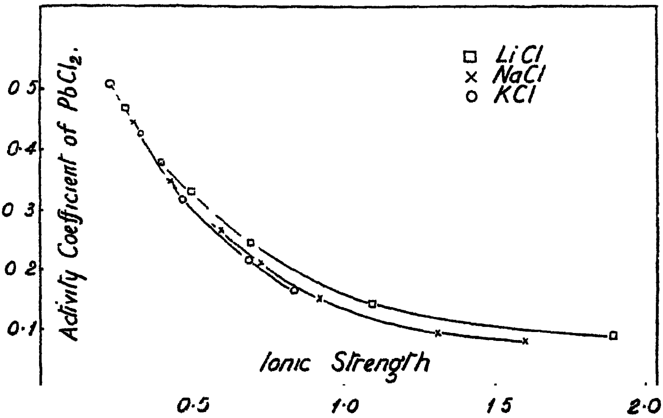

FIG. 1.

$$\gamma_{\mathrm{Pb^{++}(LiCl)}} > \gamma_{\mathrm{Pb^{++}(NaCl)}} > \gamma_{\mathrm{Pb^{++}(KCl)}}.$$

The explanation of this may be the same as that given by Harned from Hückel's theory of concentrated solutions, whereby the activity coefficients of electrolytes at a given concentration are greater in the solution possessing the higher electrical field strength, this being for the alkali chlorides in the order LiCl > NaCl > KCl. On the other hand Harned's results for hydroxides are in the opposite order. In the case of lead ions complex ion formation may play a part. The activity coefficient indicates not only the departure of the ions from behaviour as perfect solutes but also includes the effect of partial ionisation, or ion association. If complex formation occurs, it appears that KCl has the greatest effect in forcing the lead ions into the complex and LiCl the least. This is supported by the fact that solid complexes are found in the KCl system and not in the other systems. As the activity-concentration curves for the alkali chlorides pass through a minimum (Harned) and the coefficients increase above unity in strong solutions, it is clear that the very low γ values for $PbCl_2$ in strong chloride solutions must be due to the contribution of the lead ion. A very rough approximation may be made as follows. The activity coefficient of KCl at 1*M* is 0·597, and on the assumption of MacInnes, that of the chloride ion may be taken at this value. Then in a mixture of 1*M* KCl and 0·0036*M* $PbCl_2$, $\gamma_{Cl'}$ will be in the neighbourhood of the same value, say 0·6. That of $PbCl_2$ by interpolation from Fig. 1 is 0·125.

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[7] MacInnes, *J.A.C.S.*, 1919, 41, 1086.

Then
$$\begin{aligned} 0{\cdot}125 &= (\gamma_{Pb^{++}} \cdot \gamma_{Cl'}^{2})^{\frac{1}{3}} \\ &= \gamma_{Pb^{++}}{}^{\frac{1}{3}} \cdot (0{\cdot}6)^{\frac{2}{3}}, \\ \gamma_{Pb^{++}} &= 0{\cdot}00062. \end{aligned}$$

However approximate the assumptions, this figure should be of the right order. Such a large deviation of the lead ion from the behaviour of a perfect solute ($\gamma = 1$) suggests a large measure of complex formation.

Crockford and Thomas [8] applied the Debye first approximation for the activity coefficient to calculate the apparent mean ionic diameters of $PbCl_2$ in solution of $Cd(NO_3)_2$. Application of the formula to these measurements gave negative values of the parameter "*a*." This is not surprising since the solutions are not dilute with respect to added chloride.

Summary.

1. The activity coefficients of lead chloride in the presence of alkali chlorides have been calculated from measurements of the E.M.F. of concentration cells.
2. The results have been compared with similar results in other systems.
3. The possibility of complex ion formation has been discussed.

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[8] Crockford and Thomas, *J.A.C.S.*, 1933, **55**, 568.

THE SOLUBILITY PRODUCT OF THALLOUS IODIDE AT 25°.

By Cecil W. Davies and Robert A. Robinson.

Received 9th March, 1937.

During an investigation of the conductivities of some thallous salts we had occasion to make conductimetric titrations involving the precipitation of thallous iodide. The solubility of this salt proved to be so high that the titrations, employing very dilute solutions, were unsuitable for analytical purposes; but by calculating the contribution of the dissolved thallous iodide to the total conductivity we found it possible to determine the solubility product of thallous iodide by a method which is superior in three respects to the usual method, in which the conductivity of a saturated solution is determined: (*a*) it does not involve the isolation of the insoluble salt freed from all adhering traces of soluble salts; (*b*) the subsequent solution of the purified salt in conductivity water, usually a tedious process, is avoided, and (*c*) each conductivity measurement leads to a separate determination of the solubility product, so that unsuspected impurities or other causes of error are unlikely to escape detection.

A 0·002859 *N*-solution of thallous acetate in water (288·54 g.) was titrated at 25° ± 0·005 with a 0·08769 *N*-solution of potassium iodide, the conductivity being measured at intervals both before and after the end-point. This occurred at 9·567 g. of iodide solution, the solution then being 0·002768 *N* with respect to potassium acetate. The second column of Table I. gives the specific conductivities at the titres recorded in the first column. Using the data of MacInnes and Shedlovsky,[1] the conductivity of the solution at the endpoint should be $304·78 \times 10^{-6}$ r.o., and assuming that the conductivity falls linearly with the titre (the ionic strength of the solution being almost constant until the endpoint is reached) the calculated conductivities given in the third column are obtained. Beyond the endpoint we have used the data on potassium iodide by Bray and McKay;[2] equivalent conductivity figures corresponding to the total ionic strength have been employed. The difference between the observed and the calculated conductivities, given in the fourth column is attributed to dissolved thallous iodide, from which the concentration of thallous iodide may be deduced. Thence the solubility product, $S_0 = f_{Tl} f_I C_{Tl} C_I$, is found (column 5), $f_{Tl} f_I$ being calculated from the limiting Debye-Hückel equation.

TABLE I.—TITRATION OF THALLOUS ACETATE SOLUTION WITH POTASSIUM IODIDE SOLUTION.

g. KI soln. added.	$\kappa \times 10^6$.	$\kappa_{calc.} \times 10^6$.	$\Delta\kappa \times 10^6$.	$S_0 \times 10^8$.
0	317·43	—	—	—
1·7774	319·63	315·08	4·55	6·43
3·8230	318·57	312·38	6·19	6·46
6·2560	319·31	309·16	10·15	6·32
7·9171	324·50	306·96	17·54	6·31
9·0079	334·61	305·52	29·09	6·28
9·9127	351·53	319·01	32·52	6·28
11·610	402·31	386·96	15·35	6·34
13·650	476·45	467·60	8·85	6·48
15·802	557·22	551·05	6·17	6·55
18·193	646·53	642·08	4·45	6·39
			Mean:	6·38

TABLE II.—TITRATION OF POTASSIUM IODIDE SOLUTION WITH THALLOUS NITRATE SOLUTION.

g. $TlNO_3$ soln. added.	$\kappa \times 10^6$.	$\kappa_{calc.} \times 10^6$.	$\Delta\kappa \times 10^6$.	$S_0 \times 10^8$.
0	314·70	—	—	—
0·4285	318·97	313·89	5·08	6·56
2·3938	316·20	310·19	6·01	6·69
5·7744	311·97	303·83	8·14	6·56
11·3200	311·68	293·38	18·30	6·60
13·8384	321·27	288·63	32·64	6·61
15·0731	331·03	295·42	35·61	6·60
18·5425	375·33	358·57	16·78	6·62
22·2437	434·21	424·15	10·06	6·67
25·6563	489·73	482·82	6·91	6·29
30·1657	563·06	557·95	5·11	6·32
			Mean:	6·55

In the second titration a 0·0021525 *N*-solution of potassium iodide (268·00 g.) was titrated with a 0·039969 *N*-solution of thallous nitrate, the calculated conductivity at the endpoint (14·625 g.) being 286·98. The solubility product was calculated as in the preceding case.

It will be seen that the concordance between the two titrations is satisfactory, the mean value of the solubility product being $6·47 \times 10^{-8}$. If the dissociation constant of thallous iodide is of the same order of magnitude as that of thallous chloride,[3] the amount of undissociated salt in the saturated solution is negligible, and the solubility of thallous iodide in water at 25° is 2·54 × 10^{-4} g.-moles per litre.

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[1] MacInnes and Shedlovsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1429.

[2] Bray and McKay, *ibid.*, 1910, **32**, 914.

[3] Onsager, *Physik. Z.*, 1927, **28**, 277.

Summary.

The application of conductimetric titrations to the determination of a solubility product is described, and the solubility product of thallous iodide at 25° is found to be 6·47 × 10^{-8}.

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THE CATALYTIC UNION OF HYDROGEN AND OXYGEN ON COPPER AND COPPER-GOLD ALLOYS.

By A. B. Van Cleave * and E. K. Rideal.

Received 11*th March*, 1937.

The general consensus of opinion as to the mechanism by which hydrogen and oxygen combine at copper and copper-oxide surfaces to form water is that the reaction proceeds through an alternate oxidation and reduction of the metal. There is, however, great uncertainty as to the detailed mechanism and to the actual reaction which is the rate determining stage in the process. Bone and Wheeler[1] found their attempts to obtain reliable velocity measurements frustrated by the fact that the formation of water was always accompanied by an independent oxidation of the surface, but they also noted that the rate of reduction of oxidised gauze was ten times as great as the rate of formation of water from electrolytic gas. Pease and Taylor[2] likewise noted the simultaneous formation of water and cuprous oxide and concluded that the oxide itself did not catalyse the combination but underwent alternate oxidation and reduction. Similar results were obtained by Larson and Smith.[3] Tedeschi[4] claimed that the reaction kinetics could be accounted for by assuming that the velocity of reduction of the oxide was the rate determining stage; but he postulated cupric oxide as being the oxide formed at 200°, whereas the oxide formed as we have noted is in reality cuprous oxide. This fact is confirmed by electron diffraction and by Murison[5] who obtained cupric oxide only at temperatures over 600° C.; prolonged heating in air at lower temperatures yielded surface films consisting of a curious mixture of cuprous and cupric oxides. Numerous studies have been made on the formation and reduction of copper oxide at low temperatures. Palmer[6] noted that the rate of oxidation was increased by the presence of hydrogen, the maximum rate being obtained for approximately equal molecular proportions of the two gases. The variability and partly autocatalytic nature of the reduction process of copper oxide and the retarding influence of water vapour, when the reduction is carried out in hydrogen at high pressures, has been recorded by some of the above investigators as well as by G. B. Taylor and Starkweather [7] and Lewis.[8]

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* Holder of 1851 Exhibition Overseas Research Scholarship.

[1] Bone and Wheeler, *Phil. Trans.*, *A*, 1906, **206**, 1.

[2] Pease and Taylor, H. S., *J. Amer. Chem. Soc.*, 1921, **43**, 2179; 1922, **44**, 1637.

[3] Larson and Smith, *ibid.*, 1925, **47**, 346.

[4] Tedeschi, *Gazz. Chem. Ital.*, 1936, **65**, 57.

[5] Murison, *Phil. Mag.*, 1934, **17**, 96.

[6] Palmer, *Proc. Roy. Soc.*, *A*, 1923, **103**, 444.

The oxidation of copper, taking place at low gas pressures by activated diffusion of oxygen through a cuprous oxide layer to the copper-cuprous oxide interface underneath with an energy of activation of 9500 cal./mol., was investigated by Wilkins and Rideal,[9] confirming the direct measurement for the diffusion of oxygen through copper oxide by Dunn.[10] Wilkins [11] studied the kinetics of the reduction of copper oxide by hydrogen at low gas pressures obtaining an apparent energy of activation of 18,000 cal./mol., which he identified with the energy of activation for the penetration of the gas into the body of the oxide. It is noted that Ward [12] obtained an energy of activation of 14·1 kg. cal./mol. for the activated diffusion of hydrogen through copper. Wilkins and Bastow [13] attempted to correlate the velocity constants of oxidation and reduction with the rate of water formation. Their results for the rate of water formation suggested that some catalytic union was taking place in addition to the oxidation reduction process. No analysis of the gas composition during combustion was made and as noted above, Palmer's investigations [6] indicate that the rate of oxidation of the metal is affected by the presence of hydrogen. It seemed desirable to re-investigate the kinetics of this reaction at low gas pressures in an attempt to separate the purely chemical reactions from the physicochemical processes of activated diffusion which might play an important rôle in determining the reaction velocity.

Experimental.

A diagrammatic representation of the apparatus is shown in Fig. 1. Pure copper catalysts in the form of spirals or hairpin loops 45 cm. long and 0·10 mm. in diameter were suspended from tungsten leads by glass covered wires in the reaction vessel A of 300 c.c. capacity, which was connected to the Pirani gauge P and small McLeod gauge at C. T is a U-tube maintained at liquid air temperatures to remove mercury, other condensible impurities and water formed during the reaction. Definite amounts of the desired gases could be admitted through the dosers D_1 and D_2 (each 1 c.c. capacity). By means of the tap S the two gases could be mixed in any desired composition in the gas burette R.

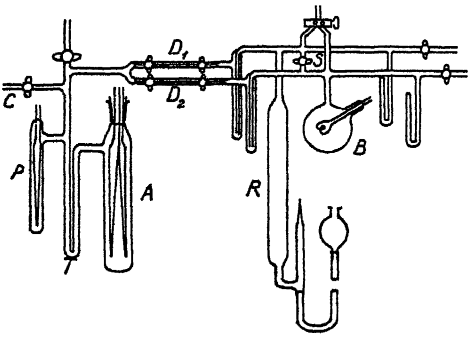

FIG. 1.—Diagram of apparatus.

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[7] Taylor, G. B., and Starkweather, *J. Amer. Chem. Soc.*, 1930, **52**, 2314.
[8] Lewis, *J. Chem. Soc.*, 1932, 820.
[9] Wilkins and Rideal, *Proc. Roy. Soc.*, *A*, 1930, **128**, 394.
[10] Dunn, *ibid.*, 1926, **111**, 210.
[11] Wilkins, *J. Chem. Soc.*, 1931, 330.
[12] Ward, *Proc. Roy. Soc.*, *A*, 1931, **133**, 506.
[13] Wilkins and Bastow, *J. Chem. Soc.*, 1931, 1525.

Hydrogen prepared from zinc and dilute sulphuric acid, after the usual purification processes, was passed into the system through a palladium tube and stored in the bulb B which was coated internally with metallic sodium. The sodium was deposited inside the bulb by electrolysis through the glass from a fused bath of a mixture of sodium nitrate and nitrite, a hot tungsten wire sealed into the bulb serving as the electron emitter for the current. Oxygen was prepared by heating recrystallised potassium permanganate and passed through a liquid air trap before use. Apiezon L grease was employed as lubricant. The Pirani gauge was calibrated for hydrogen and a series of hydrogen oxygen mixtures and, over the range employed (0-150 × 10^{-3} mm.), the square of the current required to maintain the filament (a nickel ribbon 30 cm. long 80μ wide and 7·5μ thick) 50° C. above the ice bath was found to be strictly proportional to the pressure. By simultaneous readings of the Pirani and McLeod gauges during a run it was possible to measure both the rate of water formation and any change in composition of the gas which might occur. The outgassing of the wire at 350° C. was carried out by heating the whole of the reaction vessel in an electric furnace which could be set to any desired temperature (170° C.-350° C.) and maintained constant to $\pm$ 0·2° as recorded by a standard mercury thermometer.

Results.

It was found impossible to obtain consistent results for the rates of alternate oxidation and reduction of the wire over the temperature range 170° C.-350° C. at gas pressures of 0·1 mm. The rate of oxidation tended to increase in each cycle whilst the reduction rate was erratic and slow but showed evidence that the reduction process was autocatalytic. It is possible that a few surface layers are readily reduced but that further reduction is hindered by the formation of a protecting layer of water molecules which diffuse but slowly to the surface.

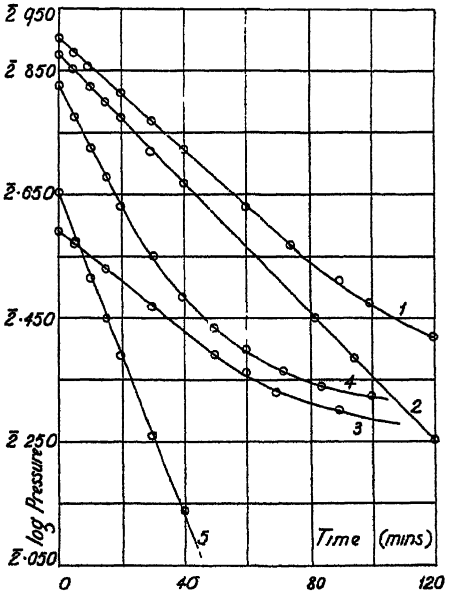

FIG. 2.—The ratio of the disappearance of hydrogen and oxygen on oxidised copper catalysts at 225° C.

Initial mixture :—

1. $2H_2 : O_2$, slightly oxidised catalyst.
2. $H_2 : O_2$, ,, ,, ,,
3. $4H_2 : O_2$, ,, ,, ,,
4. $H_2 : O_2$, strongly ,, ,,
5. $2H_2 : O_2$, ,, ,, ,,

In a hydrogen oxygen mixture (2 : 1) on the other hand, after about 20-30 minutes reaction it was found that the surface of the wire became visibly oxidised to a dull reddish colour and perfectly consistent runs could be obtained over the temperature range 170° C.-250° C. It was found that the reaction followed a first order law with respect to the total pressure, provided that too high pressures (< 0·12 mm.) were not employed and that the trap was surrounded by liquid air. That some inhibition due to water vapour formed in the reaction occurred at high pressures was confirmed by a marked diminution in velocity from $t_{\frac{1}{4}} = 20{\cdot}1$ to $t_{\frac{1}{4}} = 26{\cdot}8$ min., on replacement of the liquid air by solid CO_2 and acetone.

Analysis of the gas showed that the ratio in which the hydrogen and oxygen were consumed was 1 : 1 and not the 2 : 1 ratio expected if water formation alone was the only reaction occurring. The same ratio (1 : 1) of gas disappearance was obtained with gas mixtures with initial ratios of hydrogen to oxygen of 1 : 1, 2 : 1, 4 : 1 respectively. The unimolecular character of the reaction persisted as long as any appreciable quantity of oxygen was left as is shown from the curves in Fig. 2.

The apparent energies of activation of the reaction were calculated from the times of quarter or half-reaction with the aid of the van t'Hoff equation

$$-\frac{d \ln K}{dT} = \frac{E}{RT^2}.$$

The results are summarised in Table I. The mean value for the apparent energy of activation is $E = 6020 \pm 700$ cal.

TABLE I.—APPARENT ENERGY OF ACTIVATION FOR A SLIGHTLY OXIDISED CATALYST.

Exp.	Initial Mixture.	Temp. °A.	$t_{\frac{1}{4}}$ (min.).	E (cal.).
60	$2H_2 : O_2$	533	11·0	5830
61	$2H_2 : O_2$	504	15·1	
68	$2H_2 : O_2$	502	15·9	5410
69	$2H_2 : O_2$	467	23·9	
71	$3H_2 : O_2$	497	15·5	5830
72	$3H_2 : O_2$	468	22·6	
75	$4H_2 : O_2$	465	21·5	6180
76	$4H_2 : O_2$	443	32·0	
78	$2H_2 : O_2$	499	14·7	5370
79	$2H_2 : O_2$	449	20·9	
113	$2H_2 : O_2$	499	17·8	6520
114	$2H_2 : O_2$	473	25·7	
116	$H_2 : 3O_2$	498	16·8	6700
117	$H_2 : 3O_2$	470	25·2	
125	$H_2 : O_2$	501	13·9	6030
126	$H_2 : O_2$	471	20·6	
127	$H_2 : 2O_2$	469	21·1	6310
128	$H_2 : 2O_2$	499	14·0	
			Mean :	6020

A series of runs, in which first the initial oxygen pressure and then the hydrogen pressure was maintained constant, revealed the fact that the rates were somewhat dependent on the ratio of the gases present being a maximum at the 1 : 1 ratio, as is shown in Table II.

TABLE II.—VARIATION OF REACTION VELOCITY WITH H_2 AND O_2 PRESSURE.

Exp.	Mixture.	Temp. °C.	$t_{\frac{1}{4}}$ (min.).	Average k.
Initial O_2 Pressure Constant.				
160	$2H_2 : O_2$	226·0	29·0	0·0238
161	$H_2 : O_2$	227·5	25·5	0·0272
162	$H_2 : 2O_2$	227·5	29·7	0·0233
163	$3H_2 : O_2$	227·5	32·5	0·0213
164	$2H_2 : O_2$	227·5	31·0	0·0230
Initial H_2 Pressure Constant.				
165	$3H_2 : O_2$	228·0	32·5	0·0213
166	$2H_2 : O_2$	227·0	31·0	0·0230
167	$H_2 : O_2$	227·0	24·1	0·0287
168	$H_2 : 2O_2$	227·0	37·1	0·0187
169	$3H_2 : O_2$	227·0	32·0	0·0216

Electron diffraction photographs of the dull red surface of the wire, apparently Cu_2O, revealed the fact that it was quite amorphous and remained so even after heating to 300° C. for fifteen hours.

The effect of producing a much thicker and less permeable layer of oxide on the surface was next examined. The oxide layer, black in colour, was formed by heating the wire to 300° C. in 10 cm. of oxygen for ten hours. Electron diffraction photographs revealed large crystals of Murison's oxide, *i.e.*, a mixture of CuO and Cu_2O, the former being in excess.

The rates of reaction were found to be uniform on a wire so treated but the gases were now found to disappear in the ratio of 2 : 1, *i.e.*, in the ratio required for the formation of water and not in the ratio 1 : 1 as on the slightly oxidised wires. In Fig. 2 are shown two curves indicating the unimolecular character of the reaction which persists as long as hydrogen is present. In Table III. are given the half-times of a series of experiments and the energies of activation calculated therefrom.

The mean value obtained is E = 8670 ± 700 cal. as compared with 6020 ± 700 cal. for the slightly oxidised catalyst.

TABLE III.—APPARENT ENERGY OF ACTIVATION ON STRONGLY OXIDISED COPPER.

Exp.	Initial Mixture.	Temp. ° A.	$t_{\frac{1}{2}}$ (min.).	E (cal.).
187	$2H_2 : O_2$	497·1	15·2	8380
188	$2H_2 : O_2$	466·4	27·0	—
189	$2H_2 : O_2$	497·1	15·4	8940
190	$2H_2 : O_2$	462·6	30·3	—
192	$2H_2 : O_2$	497·1	14·1	8170
193	$2H_2 : O_2$	467·6	23·8	—
194	$2H_2 : O_2$	465·1	26·2	9200
195	$2H_2 : O_2$	497·1	13·5	—

Experiments carried out maintaining first the hydrogen and then the oxygen pressure constant, as is shown in Table IV., reveal the fact that the maximum rate of water formation, as in the case of the wire with the thin layer of amorphous cuprous oxide, occurs when the gas ratio is 1: 1.

It has been mentioned that consistent results were only obtained on a freshly reduced copper wire after a reaction period of some 30 minutes had elapsed during which period a visible film of amorphous cuprous oxide had been formed. During this interval the reaction rate shows a continuous increase and it seemed desirable to attempt to evaluate the apparent energy of activation for a freshly reduced copper wire when the reaction is proceeding relatively slowly. The catalyst was completely reduced in hydrogen at 225° C. and the system was evacuated. On admission of a 2 : 1 hydrogen oxygen mixture the course of the reaction was followed for 5 or 6 minutes and the experiment repeated. It was found, as on the slightly oxidised wire, that the gases disappeared in the ratio of 1 : 1; the apparent energy of activation, however, was found to be much higher, *viz.*, 12,800 ± 1000 cal. as is shown in Table V.

TABLE IV.—VARIATION OF REACTION VELOCITY WITH THE O_2 AND H_2 PRESSURE.

Exp.	Initial Mixture.	Temp. ° C.	$t_{\frac{1}{2}}$ (min.).	Average k.
Initial H_2 Pressure Constant.				
226	$H_2 : O_2$	223·0	17·2	0·0166
227	$H_2 : O_2$	222·5	17·0	0·0168
228	$H_2 : 2O_2$	222·9	22·5	0·0127
229	$2H_2 : O_2$	224·0	18·0	0·0158
230	$3H_2 : O_2$	224·8	18·8	0·0152
231	$H_2 : O_2$	223·9	17·0	0·0168
Initial O_2 Pressure Constant.				
232	$H_2 : O_2$	224·0	17·0	0·0168
233	$H_2 : 2O_2$	224·0	19·8	0·0144
234	$2H_2 : O_2$	224·2	20·8	0·0137
235	$3H_2 : O_2$	224·2	24·0	0·0119
236	$H_2 : O_2$	224·2	17·3	0·0165

Experiments were also carried out with gold wires and with both ordered and disordered copper gold alloys of composition Cu_3Au, kindly provided by Dr. C. Sykes of Metropolitan Vickers Ltd., whom the authors have to thank. The order in the ordered wire formed by heating to 380° C. for 100 hours and cooled at the rate of 10° per hour was checked by X-ray photograph. The gold wire 90 cm. long and 0·10 mm. diameter was cleaned, outgassed at 380° C. and examined for catalytic activity in a 2 : 1 mixture at 0·1 mm. pressure up to a temperature of 350° C. The gold was found to be catalytically inert, a preliminary consumption of a small quantity of oxygen presumably due to a trace of some impurity, probably carbon, alone being observed.

Both the ordered and disordered alloys behaved in a similar manner. In a 2 : 1 gas mixture only oxygen was consumed and the gas formed was identified as carbon dioxide. When carbon dioxide approximately equivalent to 0·01 per cent. carbon in the alloys had been formed, a slow oxidation of the wires commenced until all the oxygen had been used up, no hydrogen being consumed. The rates of oxidation of the alloys were much more reproducible than that for pure copper and the rate of oxidation was found to be the same in pure oxygen as in hydrogen oxygen mixtures as is shown in Fig. 3.

TABLE V.—THE APPARENT ENERGY OF ACTIVATION ON REDUCED COPPER.

Exp.	Initial Mixture.	Temp. ° A.	$t_{\frac{1}{2}}$ (min.).	E (cal.).
199	$2H_2 \ O_2$	497·2	34·8	13,100
200	$2H_2 \ O_2$	467·1	82·0	—
202	$2H_2 \ O_2$	495·6	39·0	12,100
203	$2H_2 : O_2$	467·1	82·0	—
207	$2H_2 \cdot O_2$	498·1	26·9	12,500
208	$2H_2 . O_2$	466·2	64·0	—
210	$2H_2 \cdot O_2$	457·2	75·0	13,300
211	$2H_2 \ O_2$	495·1	24·5	—
212	$2H_2 \cdot O_2$	495·1	24·5	12,900
213	$2H_2 \cdot O_2$	465·1	57·0	—
			Mean :	12,760

The apparent energy of activation for the formation of oxide on the ordered alloy was found to be E = 8600 ± 1000 cal. both in oxygen and hydrogen-oxygen mixtures, and the oxide formed was found to be very resistant to reduction by hydrogen, which was only detectable when all the oxygen in the mixed gases had been consumed. For the disordered alloy the general behaviour was the same with a similar energy of activation, *viz.*, $E = 8900 \pm 1000$ cal. Since both these catalysts behaved so very differently from pure copper it was decided to extend the investigations to alloys richer in copper. Hence, two alloys in the form of wires analysing Cu_4Au and Cu_9Au were prepared by Johnson Matthey Ltd.

It was found that the Cu_4Au alloy behaved in a manner similar to the ordered and disordered Cu_3Au systems, that is, a comparatively slow reaction took place in which all the oxygen disappeared followed by an extremely slow reduction. However, if the catalyst was deliberately oxidised by heating in oxygen at 230° C. for five minutes, the wire showed a catalytic activity, for, in both a 2 : 1 and 1 : 1 mixture the rate of reaction was constant until approximately two-thirds of the gases had reacted when the velocity began to fall but the reaction proceeded to completion, the catalyst becoming

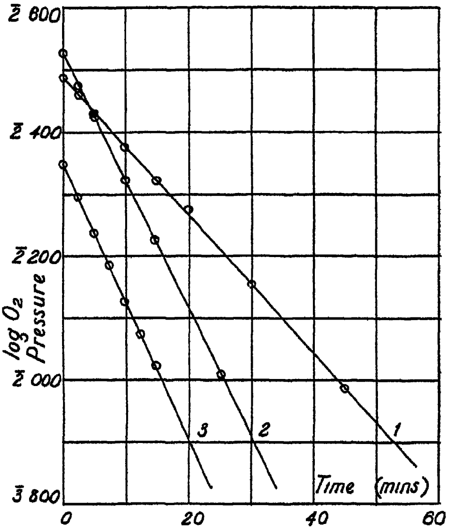

FIG. 3.—Rate of reaction on Cu_3Au catalysts.

1. Initial mixture $H_2 : O_2$, 310° C.
2. „ „ $H_2 : O_2$, 344° C.
3. „ „ pure O_2, 346° C.

covered with a reddish-brown oxide. On admission of hydrogen at 234° C. to the catalyst in this state, a very rapid reduction of the oxide took place. The apparent energy of activation for the catalytic reaction was found to be $E = 9800$ cal., of the same order as that obtained on the heavily oxidised copper wires.

For the Cu_9Au wire the behaviour was somewhat similar. Without a preliminary oxidation of the wire only oxygen was consumed from hydrogen oxygen mixtures but after a preliminary oxidation both gases disappeared as shown in Fig. 4. The energy of activation in the oxisded wire was found to be 8100 ± 1000 cal.

The oxidised Cu_9Au wire like the Cu_4Au alloy was, in contrast to oxidised copper, very easily reduced, the rates of reduction of the three wires after identical extents of oxidation being shown in Fig. 5.

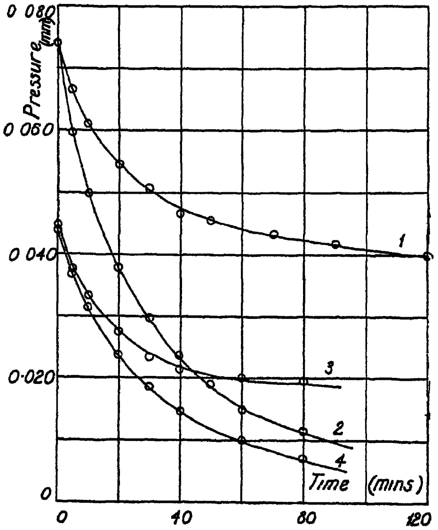

FIG. 4.—The ratio of the disappearance of hydrogen and oxygen on Cu_9Au.

Initial mixture :—

1. $2H_2 : O_2$, reduced catalyst, 235° C.
2. $2H_2 : O_2$, oxodised catalyst, 235° C.
3. $H_2 : O_2$, reduced catalyst, 229° C.
4. $H_2 : O_2$, oxidised catalyst, 229° C.

Discussion.

The experiments described above indicate that there may be three different processes which control the rate of water formation from hydrogen and oxygen in the presence of copper. Commencing with copper reduced in hydrogen, the energy of activation is found to be 13·1 Kg. cal. in close agreement with the value 14·0 Kg. cal. found by Ward [12] and Melville and Rideal [14] for the energy of activated diffusion of hydrogen into copper. The results indicate that this is the rate controlling process, *i.e.*, reaction can only occur after chemi-adsorption of oxygen on places vacated by the hydrogen. A similar energy of activation [13] is to be anticipated in the reduction reaction where copper oxide is protected by a layer of reduced metal through which hydrogen has to diffuse.

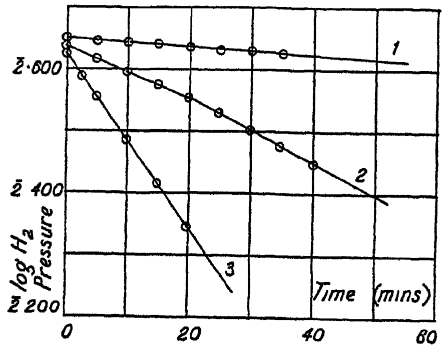

FIG. 5.—The rate of reduction of oxidised catalysts by hydrogen.

1. Pure copper, 348° C.
2. 90 atomic per cent. copper, 227° C.
3. 80 atomic per cent. copper, 234° C.

At a slightly oxidised copper surface, on the other hand, both gases are chemi-adsorbed, reaction takes place between them and the rate of water formation is at a maximum. It is important to note that this reaction, which has an energy of activation of approximately 6 Kg. cal., and the preceding reactions are coupled reactions which may be formally expressed by the equation :

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[14] Melville and Rideal, *Proc. Roy. Soc., A*, 1935, **153**, 77.

$$Cu_x + H_2 + O_2 \rightarrow Cu_2O + Cu_x + H_2O,$$

where Cu_x represents solid copper. Since the oxide formed during the reaction is cuprous oxide the reaction might be expressed by the following sequence :

$$Cu_x + O_2 \rightarrow Cu_xO_2$$
$$Cu_x + H_2 \rightarrow 2CuH + Cu_x$$
$$Cu_xO_2 + 2CuH \rightarrow Cu_x + Cu_2O + H_2O.$$

In order that the chemi-adsorption of hydrogen may continue, the oxygen retained as cuprous oxide has to diffuse away into the underlying copper and the activated migration of this oxygen may well be the rate determining step. The oxidation of the substrate is attended by an increase in volume and in consequence relatively deep layers of the copper may be attacked to form cuprous oxide. It is for this reason that the coupled reaction on the hydrogenated copper is gradually transformed to this coupled reaction as the hydrogenated layers are consumed. The above formulation also makes it clear why Murison's oxide contains cupric as well as cuprous oxide.

When the oxide layer on the surface has become relatively thick and contains a large percentage of cupric oxide (produced by prolonged oxidation at 300° C.) the copper substrate ceases to be effective as an absorber of migrating oxygen and the oxide functions as a true catalyst, *i.e.*, hydrogen and oxygen disappear in the ratio of 2 : 1. It is significant that the energy of activation of this process is that usually associated with the activated diffusion of oxygen through copper oxide, *viz.*, 9·0 Kg. cal. and it suggests that this process of diffusion may be regarded either as the migration of oxygen atoms or the alternate formation of cuprous and cupric oxides according to the equation

$$Cu_2O \rightleftharpoons Cu + CuO.$$

As before, copper nuclei here set free by the migrating oxygen serve as hydrogen donors, *i.e.*, are points on which hydrogen (or oxygen) can be chemi-adsorbed. The chemi-adsorbed hydrogen being relatively immobile is attacked by the migrating oxygen, which is incorporated in the oxide forming the Murison layer, and is renewed by chemi-adsorption on bare copper atoms. In the steady state, the first few layers of oxide will be mainly in the cuprous condition through which the oxygen migrates until it reacts with chemi-adsorbed hydrogen.

From the experiments on the alloys it is noted that the process of oxidation is scarcely affected by the presence of the gold, the energy of activation obtained being almost the same as that for pure copper, *i.e.*, the controlling factor is the activated migration of the oxygen. This observation lends support to the view that the activated migration of oxygen through cuprous oxide to the copper oxide interface takes place by atoms rather than by molecules of oxygen. On the other hand the coupled reaction and the reduction of slightly oxidised alloy wires is practically completely repressed. It appears probable that the surface layers of all these wires must be rich in gold, the layers being permeable to oxygen but not to hydrogen. When the surface layers are broken up by the expansion of the underlying copper when oxidised, the alternate reduction and oxidation of the copper oxide is facilitated by the presence of the gold and a true catalytic process through alternate oxidation and reduction can take place, the controlling process being in all cases the rate of activation for migration of the oxygen in the copper oxide and not the rate of chemi-adsorption of the hydrogen.

These experiments do not throw any direct light on the mechanism by which the gold facilitates the reduction of the cuprous oxide but, as noted above, it is possible that since chemi-adsorption of hydrogen only occurs on the copper and not on the oxide, the gold as well as copper may be acting as a chemi-adsorbent for hydrogen, the former possessing the advantage of not being susceptible to poisoning for the chemi-adsorption of hydrogen by oxygen.

Summary.

In the interaction of hydrogen and oxygen in the presence of copper three distinct reactions have been identified, two of which are coupled reactions involving the formation of a molecule of cuprous oxide for every molecule of water formed. The energies of activation for the reactions are 13·0 and 6·0 Kg. cal. respectively. The controlling factor in the first reaction is believed to be the activated migration of hydrogen and in the second the activated migration of oxygen. The true catalytic union of hydrogen and oxygen only occurs on oxidised surfaces with an energy of activation of 9 Kg. cal. Reasons are given for the supposition that the activated diffusion of oxygen involves the transitory conversion of a molecule of cuprous oxide into one of cupric oxide and a free copper atom, and that copper or some other metal preferably not poisoned by oxygen is required for the chemi-adsorption of hydrogen. At least two contiguous atoms are required for the chemi-adsorption of molecular hydrogen.

These views receive some support by observations on the reactions of hydrogen and oxygen on a series of gold copper alloys.

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THE ELECTROPHORETIC MOBILITY OF PURIFIED TRISTEARIN. PART II. THE ALKALINE REGION.

By A. L. Roberts.

(*Communicated by* W. C. M. Lewis, F.R.S.)

Received 26th February, 1937.

In a previous paper [1] an account of the electrophoretic behaviour of aqueous dispersions of purified tristearin was given, but the measurements made were entirely restricted to the acid side of neutrality. These measurements have now been extended and the greater part of the work which is here described has been on the alkaline side of p_H 7. The importance of the examination of the mobility of the fat in the alkaline region was clearly indicated by the remarkably strong effect of variations in the p_H upon it, as compared with the effects of variations in the concentration of neutral salts.

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[1] Roberts, *Trans. Faraday Soc.*, 1936, 32, 1705.

The purification of the tristearin, the preparation of the dispersions and the experimental method of measuring the mobility were described in the previous paper.

(*a*) The Effect of p_H on Tristearin Dispersions in the Presence of the Sodium Ion.

Because of the importance of the hydrogen (or hydroxyl) ion concentration in determining the mobility, which has been shown in the previous work, the observations at different values of the p_H above 7 have been carried out at three concentrations of sodium salt, *viz.* 0·01N, 0·005N and 0·002N. The measurements were made mainly in solutions of sodium borate buffer because, by the use of this, the p_H was more readily adjusted, and also more exactly measured, than in unbuffered solutions. It is not to be expected that the introduction of the borate ion into the dispersions will cause any complications in the mobility results, for it will be seen from Part I. that, at the same normality, the particular nature of the added anions, apart from the hydroxyl ion, is immaterial in so far as the mobility is concerned.* It seemed advisable, however, to confirm this conclusion in the alkaline region. Therefore, a few points have been determined in sodium chloride—caustic soda mixtures in which the total sodium ion concentration was the same as in the buffer solutions. Owing to the difficulties in the use of the hydrogen electrode method of p_H measurement in poorly buffered solutions, the number of these points has been necessarily restricted. They are plotted with the borate results in Fig. 1.

The borate buffer employed was a 0·1N with respect to caustic soda and 0·2M with respect to boric acid. It was diluted to give the required concentration of sodium ion with dispersion or distilled water as necessary. For values of the p_H between 9 and 7, to this buffer were added suitable quantities of dilute hydrochloric acid, while above p_H 9 the sodium borate buffer was progressively replaced by the equivalent amounts of caustic soda solution necessary to maintain the concentration of the sodium ion constant. In the case of the sodium chloride—caustic soda results the value of the p_H was raised by the replacement of the salt by the corresponding amount of sodium hydroxide solution. The values of the p_H were measured in all cases by the glass electrode below p_H 9, and by the hydrogen electrode for more alkaline solutions. These measurements were accurate to 0·01 unit.

The mobility determinations were made at 25° C., and Fig. 1, in which the points on the acid side of p_H 7 are taken from the previous paper and represent measurements in hydrochloric acid—sodium chloride mixtures, shows the results obtained. The strong charging effect of the increasing hydroxyl ion concentration is at once apparent, but probably the most surprising result is the relatively small effect of alteration in the sodium salt concentration upon the mobility at a given value of the p_H. On the alkaline side of neutrality the mobility decrease due to increasing the sodium salt concentration is approximately the same for any value of the p_H, while on the acid side the effect becomes less and less until below p_H 3 it is negligible. With regard to the effect of the hydroxyl ion, clearly, above p_H 9 a state of saturation of the surface is being attained for this ion. This may be due to the adsorption of the hydroxyl ion from the bulk of the aqueous phase or to the removal of hydrogen ion from the rigidly adsorbed secondary ion shell. The process, however, is not simple. It is plain that the fall in the mobility with increasing concentration of the sodium ion is far from great enough to justify the assumption of a constant electrokinetic charge density even at the highest values of the p_H examined, as will be seen from the charge density tables given later. Furthermore, at the higher values of the p_H particularly, the borate ion is present to a considerable extent in the multivalent form and this too must cause an alteration in the electrokinetic charge density, although this is not reflected in the mobility, as compared with the simpler case of the univalent chloride ion.

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* In addition to the salts already mentioned in Part I., measurements of the mobility have also been made in KCNS and K_2SO_4 at p_H 4 and the results were identical with those for KCl at this p_H.

In Part I. of this paper it was observed that the substitution of one alkali metal cation for another produced a small but noticeable alteration in the mobility value. The mobility decreases as the alkali metal ion series was ascended from lithium to cæsium. This decrease was small and appeared to be approximately independent of the value of the p_H. In order to confirm this result a couple of measurements were made on the alkaline side of neutrality in $N/100$ cæsium borate buffer instead of sodium borate. These points lie roughly on the same curve as the sodium points and, making allowance for experimental error, it seems likely that the effect of this substitution is no greater than that found on the acid side, *i.e.* about one mobility unit.

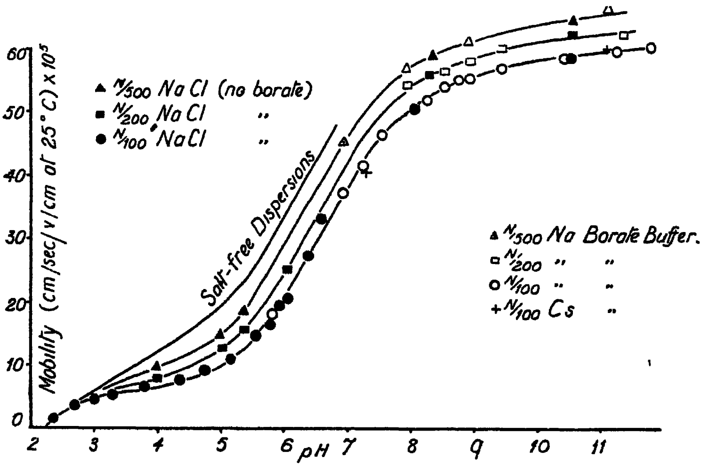

FIG. 1.—The electrophoretic mobility of tristearin in sodium salt solution.

(b) The Effect of p_H on Tristearin Dispersions in the Presence of the Barium Ion.

It is well known that the barium ion is far more effective in reducing the mobility of a negatively charged substance than are the alkali metal ions, and it is of interest to observe the modification of the curves in Fig. 1 produced by the substitution of the barium ion for that of sodium. A series of measurements was made in 0·01N, 0·005N and 0·002N barium borate solutions. The p_H adjustments were made in a similar manner to those for the case of sodium. Between p_H 9 and 7 increasing amounts of hydrochloric acid were added to the barium borate and above p_H 9 the borate was progressively replaced by barium hydroxide. The p_H measurements were made by the same methods as above, by the glass electrode method for the lower values and by the hydrogen electrode in the more alkaline solutions. In order to make the curves more complete a few points have also been obtained on the acid side of p_H 7 in the presence of barium chloride at similar concentrations to those points above 7, the required values of the p_H in these cases being obtained by adding hydrochloric acid.

Fig. 2, which illustrates the results, shows at once the much more powerful discharging effect of the barium ion as compared with the sodium ion. It will also be seen that the depression of the mobility is mainly produced by the first additions of the salt. The difference between the mobility—p_H curve for the electrolyte-free case and that for 0·002N barium salt solutions is far greater than any subsequent fall resulting from a further increase in concentration of the salt to 0·01N.

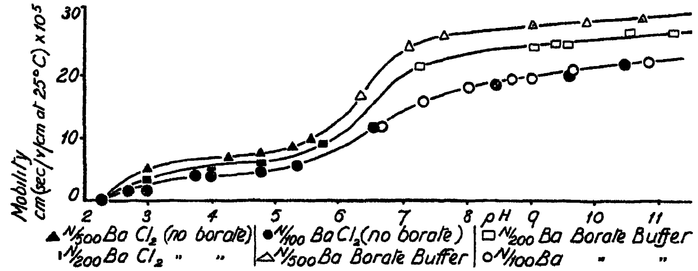

FIG. 2.—The electrophoretic mobility of tristearin in barium salt solution.

In spite of the much reduced mobilities in the barium salt solutions as compared with those in sodium salt solutions, however, the effect of the p_H upon the mobility is by no means absent. Once again, from p_H 5 to 8 there is a comparatively rapid rise in the mobility followed by the approach to a maximum value above p_H 9.

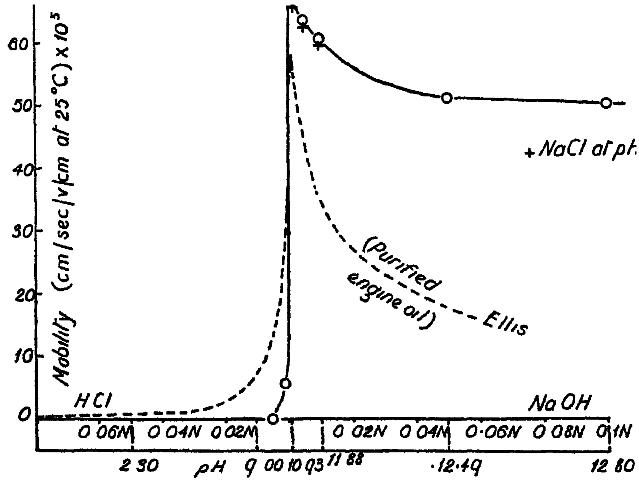

FIG. 3.—The effect of acid and alkali on the mobility of tristearin dispersions.

(c) The Effect of Increasing Concentration of Caustic Soda on the Mobility of Tristearin Dispersions.

It was observed by Ellis [3] that on adding caustic soda to water containing suspended droplets of purified engine oil, a hydrocarbon, the mobility first increased, then after passing through a maximum finally fell without, however, reaching zero. This effect is clearly due to the charging effect of the hydroxyl ion coupled with the discharging effect of the increasing cation concentration. At first the former outweighs the latter but apparently the surface rapidly tends towards a saturated state with respect to the hydroxyl ion and then the sodium ion, by closing in the double layer, is able to reduce the mobility. For comparison with these results of Ellis a similar set of measurements was made on tristearin dispersions. The dispersions were examined in various concentrations of caustic soda * up to $0{\cdot}1N$. It is interesting to note that, in the case of tristearin, whilst the alkali does not produce such a strong depression as Ellis observed for his hydrocarbon, on the acid side the mobility of the fat falls off much more rapidly than that of the engine oil. The curve found by Ellis and that for tristearin are compared in Fig. 3.

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[3] Ellis, *Z. physik. Chem.*, 1912, 78, 321.

Discussion.

In the previous paper it was concluded that the main controlling factor in determining the mobility of tristearin was the value of the p_H and the work which has now been carried out in the alkaline region has completely justified this view. The results obtained show that, whilst anions other than the hydroxyl ion affect the mobility, and hence ζ, to the same extent at equal normalities, the rôle of the hydroxyl ion is quite unique. It will also be observed that most of the effect of this ion is manifested whilst its concentration is still very small. For example, an increase in p_H from 2·2 to 9·0, corresponding to a rise in the bulk concentration of the hydroxyl ion from $1{\cdot}6 \times 10^{-12}$ N to 1×10^{-5} N, causes an increase in the electro-phoretic mobility in $N/100$ sodium salt from 0 to $55{\cdot}7 \times 10^{-5}$ cm./sec./v./cm. but a further rise in the concentration of this ion to approximately 1×10^{-2} N raises the mobility only a further five units. From Fig. 3, which shows the effect of increasing concentration of caustic soda on the mobility of the dispersions, the mobility is seen to rise very rapidly to a maximum value, at a concentration between 0·001 N and 0·002 N caustic soda, after which the curve falls in a manner entirely analogous to that observed for neutral sodium and potassium salts. Indeed, it is possible to read off from Fig. 1 three values of the mobility at, say, p_H 11 in the presence of increasing sodium salt concentration, and it is found that these points fall close to the declining part of the mobility—caustic soda concentration curve. It may be said, therefore, that slight variations in the concentration of the hydroxyl ion produce very strong effects at low bulk concentrations, but a limiting concentration is reached above which the effect of further additions of this ion may be said to be "normal." The "normal" behaviour of anions is that they affect the mobility to the same extent at the same normality and value of the p_H independently of their valency or of the p_H at which the comparison is made.

The inference to be drawn from this is obvious. It appears that initially, on increasing the hydroxyl ion concentration in the dispersions, this ion plays a part in the formation of the double layer system which is not available to any of the other anions which have been examined.

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* For the moving boundary method of mobility determination it is not usual to use solutions of such concentrations as $0{\cdot}1N$, because of their high conductivity and the consequent heating effect which causes convection currents in the U-tube. As a result of the high mobility of the fat in caustic soda solutions, however, it is possible in this case to use a low potential gradient, 0·3 v./cm., and convection currents do not occur.

Once this initial effect has exhausted itself, further additions of anions, whether hydroxyl or not, are accompanied by a variation in the electrophoretic mobility which is independent of the nature of the added anion.

Although it is necessary to attribute a specially strong adsorbability to the hydroxyl ion as compared with other anions, in order to explain the results of the observations which have been made, the value of the electro-kinetic charge density is markedly affected by all anions, as the charge density table shows, even at the highest values of the p_H. If, however, it be assumed that all anions can rigidly adsorb on to the fat surface the surprising fact is that all of these anions apparently affect the mobility, and ζ, to the same extent at the same normality.

The behaviour of the different anions from the standpoint of the electro-kinetic charge density, however, is much more complicated than from that of the mobility. The electro-phoretic charge density is affected by the valency of the anion and is the greater, at the same normality, the greater the valency of the anion present. If, instead of considering the same number of negative charges per unit volume, we take the same number of anions per unit volume the difference in behaviour is even more marked. For the polyvalent anion, even allowing for the extra depressing effect of the necessarily increased number of cations, the charge density is found to be much greater than for the univalent ion.

TABLE I.—THE ELECTRO-KINETIC CHARGE DENSITY, σ, IN e.s.u./$cm.^2$.*

p_H.	Charge Density. Conc. of Positive Ion.			
	Nil.	0·002*N*.	0·005*N*.	0·01*N*.
In Uni-univalent Sodium Salt Solutions.				
11·0	—	2670	3870	5180
10·0	—	2590	3800	5070
9·0	—	2500	3650	4850
8·0	—	2330	3380	4370
7·0	—	1870	2640	3290
6·0	61	1090	1480	1790
5·0	82	600	770	870
4·0	125	420	490	630
3·0	160	250	320	440
2·2	0	0	0	0
In Barium Salt Solutions with a Univalent Anion.				
11·0		1470	2090	2400
10·0		1440	2020	2240
9·0		1400	1950	2090
8·0		1340	1850	1900
7·0		1200	1530	1540
6·0		640	830	840
5·0		400	510	530
4·0		320	380	410
3·0		250	250	250
2·3		0	0	0

* The values given in this table are calculated from the smoothed mobilities; those below p_H 7 are included to make the table more complete, being taken from the previous paper. The expression for σ which has been employed throughout is that due to Henry.[3]

With respect to the effect of the different cations upon the electro-kinetic properties of the fat, it is again the valency of the ion which appears to be the important controlling factor. It has been found that the substitution of the sodium ion by the cæsium ion is almost without effect upon the mobility and its related properties, but that the introduction of the barium ion is accompanied by an immediate fall in the mobility to approximately half its value in the same normality of the sodium salt.* The actual ratio of the mobility in barium salt to that in sodium salt of the same normality is dependent upon the p_H at which the comparison is made. The table shows that the electrophoretic charge density is also much less in the case of the barium salt solutions than it is in the corresponding sodium salt solutions. Although the barium ion is more effective than are the alkali metals, however, it is incapable of masking the effect of p_H. The mobility of the dispersions falls to the value zero, at p_H 2·2 to 2·3, irrespective of whether there be any salt present or not. The form of the mobility—p_H curves in the presence of barium salt also does not differ fundamentally from that in sodium salt solution.

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[3] Henry, *Proc. Roy. Soc., A*, 1931, **133**, 124.

The above statement, that cations of the same valency have a very similar effect, must be modified in the case of the hydrogen ion. The concentration of this ion is, of course, inseparably bound up with that of the hydroxyl ion and it is impossible to distinguish completely between the effects of the two. If, however, a strong primary specific adsorbability be ascribed to the hydroxyl ion, an analogous secondary adsorbability must be attributed to the hydrogen ion to account for the low values of electro-kinetic charge density σ found in the absence of added salts. The increase in σ on the addition of salts must then be a result either of primary adsorption of the anion added or of a loosening of some of the hydrogen ions which are assumed to be rigidly held (in the secondary layer). As σ is also strongly affected by the valency of the cation it will be seen that the problem of the factors which determine it is a very complex one. This exceptional adsorbability on the part of the hydrogen and hydroxyl ions is not restricted to tristearin. The effectiveness of the hydrogen ion in reducing the charge on a surface was observed by Perrin [4] for several substances. It has also been noticed particularly in the case of hydrocarbons, *e.g.*, compare the effect of hydrochloric acid on the engine oil used by Ellis [2] with the effect of the alkali metal chlorides as found by Powis [5] using the same oil; see also the work of Tuorila [6] and Limburg.[7]

Note on the Stability of Tristearin Dispersions.

Measurements have been made for the work recorded in this and the previous paper on tristearin dispersions in which the electrophoretic mobilities varied between 0 and $67{\cdot}0 \times 10^{-5}$ cm./sec./v./cm. It is clear, of course, that many of the dispersions used must have been unstable but fortunately, all were sufficiently stable to survive the hour necessary to carry out a determination. The actual stability may be summed up as follows :—

(*a*) The ordinary stock dispersions in water, p_H approximately p_H 6, were stable indefinitely.

(*b*) In the absence of added salts the dispersions at p_H 4 separated partially after twenty-four hours and more or less completely after two to three days. Below p_H 4 coagulation was complete within twenty-four hours.

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* It may be considered that the barium and sodium ions would be better compared at the same molarity rather than at the same normality. A glance at the curves for *N*/200 sodium salt and for *N*/100 (*M*/200) barium salt, respectively, shows that no radical change in the results is involved as a consequence of such a change in viewpoint.

[4] Perrin, *J. Chim. physique*, 1904, **2**, 601.

[5] Powis, *Z. physik. Chem.*, 1915, **89**, 91.

[6] Tuorila, *Kolloidchem. Beih.*, 1928, **27**, 44.

[7] Limburg, *Rec. Trav. chim. Pays-Bas*, 1926, **45**, 854.

(*c*) In sodium chloride solution the dispersions were stable above p_H 43· in all cases. At p_H 4·3 and below those containing $N/100$ or $N/200$ salt had separated after twenty-four hours. In $N/500$ sodium salt the dispersion at p_H 4·3 was stable but that at 4·0 separated partially after twenty-four hours and totally within two days.

(*d*) In barium salt solutions all dispersions except those at the very highest p_H values were relatively unstable. Dispersions containing $N/100$ $Ba(OH)_2$ or $N/200$ $Ba(OH)_2$ coagulated partly after three days and totally after one week, but that containing $N/500$ $Ba(OH)_2$ was stable indefinitely. Below p_H 8 all of the dispersions had separated after twenty-four hours.

These results give the maximum values of the ζ-potential at which coagulation occurs as :—

HCl alone	18 mv.	$N/500$ Ba salt	33 mv.
HCl + $N/500$ NaCl	12 mv.	$N/200$ Ba salt	33 mv.
HCl + $N/200$ NaCl	11 mv.	$N/100$ Ba salt	28 mv.
HCl + $N/100$ NaCl	10 mv.		

Whilst there is some degree of constancy in the values for the same salt there appears to be no simple relation between those for the different salts.

Summary.

(1) The electrophoretic mobility of purified tristearin has been determined as a function of p_H in sodium salt solutions at different concentrations on the alkaline side of neutrality.

(2) The mobility has also been found, mainly on the alkaline side of p_H 7 as a function of p_H in barium salt solutions of different concentrations.

(3) It is observed that the replacement of the borate anion by an equivalent amount of the chloride ion is without effect upon the mobility at any given value of the p_H.

(4) The effect of increasing concentration of caustic soda upon the mobility of tristearin has been observed.

(5) It is found that the barium ion is more effective in reducing the mobility at any value of the p_H than are the alkali metal cations.

(6) It is concluded that variations in the concentration of the hydroxyl ion are very effective upon the mobility and that in this respect the hydroxyl ion is unique. On increasing its concentration, however, a point of saturation is rapidly attained, after which its behaviour becomes normal.

(7) It is also concluded that the hydrogen ion is capable of strong adsorption in the secondary rigid (Helmholtz) layer.

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THE PARTIAL MOLAL VOLUME OF WATER AND DEUTERIUM OXIDE IN DIOXAN SOLUTION.

BY R. A. ROBINSON AND R. P. BELL.

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Since the equilibrium configurations of isotopic molecules are independent of the mass of the isotope, their partial molal volumes in a condensed system will to a first approximation be identical. Actually, however, there should be a small difference arising from the different zero point energies which will affect the distance of closest approach between two molecules and hence the molal volumes. This difference has been detected in a number of cases involving the isotopes of hydrogen; thus, the molal volume of D_2 is 11 per cent. less[1] than that of H_2, solid LiD has a molal volume 1·5 per cent. less[2] than LiH, the molal volume of C_6D_6 is 0·21 per cent. below[3] that of C_6H_6 and a similar[4] difference of 0·3 per cent. is found for solid D_2O and H_2O. In general it is found that, in agreement with theory, a compound containing deuterium has a somewhat smaller molal volume than the corresponding hydrogen compound. In the case of water, however, while the difference between the two kinds of ice is in this sense, the molar volume of liquid D_2O is 0·3 per cent. *greater*[5] than that of liquid H_2O. It is possible that the reversed effect is due to the peculiar pseudocrystalline structure of water since the higher freezing-point of D_2O indicates that it tends more to the open ice-like structure postulated by Bernal and Fowler. This structural effect could be eliminated by measuring the partial molal volumes of D_2O and H_2O in dilute solution in a non-hydroxylic solvent, since any interaction between the solute molecules will be absent at infinite dilution. The present paper describes such measurements for solutions in dioxan (diethylene dioxide). This solvent is completely miscible with water and has been used previously in an investigation of the osmotic coefficients of D_2O and H_2O in solution.[6]

TABLE I.

No.	Per Cent. Solute.		d_4^{25}.	ϕ.
	By Wt.	By Mols.		
H_2O as Solute.				
3a	0·1982	0·962	1·02765	17·27
2a	0·5734	2·742	1·02771	17·26
3b	0·6101	2·913	1·02773	17·22
2b	0·9283	4·380	1·02780	17·20
1a	1·3849	6·423	1·02792	17·16
2c	1·6616	7·630	1·02805	17·09
3c	2·2475	10·103	1·02826	17·05
1b	2·7298	12·064	1·02848	16·99
1c	3·2412	14·071	1·02782	16·95
1d	3·7541	16·013	1·02896	16·92
3d	4·0803	17·214	1·02916	16·89
D_2O as Solute.				
1a	0·1906	0·834	1·02786	17·07
2a	0·2946	1·285	1·02797	17·21
1b	0·4206	1·826	1·02815	17·07
2b	0·7495	3·219	1·02852	17·17
2c	0·9932	4·231	1·02886	17·10
1c	1·5237	6·380	1·02956	17·05
1d	2·2100	9·053	1·03047	17·02
2d	2·6403	10·669	1·03099	16·98
1e	3·3085	13·096	1·03208	16·91
1f	4·3540	16·700	1·03367	16·84

Experimental.

Commercial dioxan was purified by the method of Oxford.[7] The density of the product was lower than that previously recorded, probably because of traces of light petroleum introduced with the sodium in the course of purification. These traces were removed by fractional freezing, yielding a product of d_4^{25} 1·02762, compared with 1·02766 found by Hovorka, Schaeffer, and Dreisbach,[8] and f. pt. 11·75°. In view of the reported instability of dioxan, we preserved samples in a dessicator over sulphuric acid for two months, some being exposed to the normal light of the laboratory and others being kept in the dark. In one case we observed an increase in density of three parts in 100,000 and in the other cases of one part in 100,000. Moreover, during the month in which this work has been done, we have exposed dioxan to the normal moisture content of the laboratory atmosphere in the course of transferring it to pyknometers, weighing bottles, etc., and in no case have we observed a change in density exceeding the experimental error.

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[1] Clusius and Bartholomé, *Physikal. Z.*, 1934, **35**, 969.

[2] Zintl and Harder, *Z. physikal. Chem.*, *B*, 1935, **28**, 478.

[3] Ingold, Raisin, and Wilson, *J. Chem. Soc.*, 1936, 915.

[4] Timmermans, Hennault-Roland, and Rozental, *Compt. rend.*, 1936, **202**, 1061.

[5] Using the value 1·1074 for the density of heavy water given by Tronstad, Nordhagen, and Brun, *Nature*, 1935, **136**, 515.

[6] Bell and Wolfenden, *J. Chem. Soc.*, 1935, 822.

[7] *Biochem. J.*, 1934, **28**, 1325.

[8] *J. Amer. Chem. Soc.*, 1936, **58**, 2264.

The deuterium oxide contained 98·9 per cent. D_2O. All solutions were made up by weight. The densities were determined in a 25 c.c. pyknometer at 25°, the estimated error being less than ± 0·002 per cent. Between each set of density measurements the value for pure dioxan was redetermined as a check.

Results.

Table I. gives the compositions and densities of the solutions measured together with the apparent molal volume ϕ defined as

$$\phi = M\{1/d - w/d_0\}/w$$

where M is the true molecular weight of the solute (corrected in the case of D_2O for the small proportion of H_2O present), w is the weight fraction of solute, d the density of the solution and d_0 the density of pure solvent.

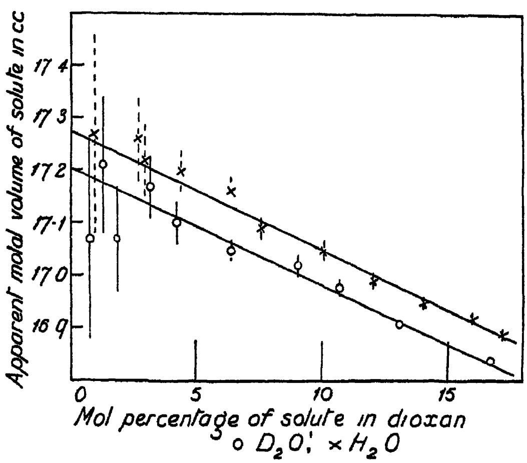

FIG. 1.

These values are plotted against the molal percentage of solute in the figure, the lengths of the vertical lines indicating the error in ϕ which results from an error of ± 0·002 per cent. in the density.

It is clear that over the whole range of concentration investigated ϕ_{D_2O} is about 0·5 per cent. smaller than ϕ_{H_2O}, this difference persisting even at infinite dilution. For both D_2O and H_2O the partial molal volume at infinite dilution is smaller than the corresponding molal volume in the liquid state, as would be expected if the pure liquids possess that open structure described by Bernal and Fowler. Moreover, the difference in volumes at infinite dilution in dioxan is in the direction which would be anticipated from the difference in the zero point energy. The order of magnitude of this difference is approximately what would be expected, a difference of about 2×10^{-10} cm. in the classical amplitudes of the zero point vibrations being predicted theoretically.

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THE SALTING OUT OF GASES AND VOLATILE NON-ELECTROLYTES.

By J. W. Belton.

Received 6th December, 1935; *and in revised form on 17th March*, 1937.

The calculation of the influence of salts on the solubility of non-electrolytes has been given by Debye and McAulay,[1] who calculated the electrical contribution to the free energy and so the activity coefficient of the non-electrolyte. A more direct derivation of the relation obtained by them has been given by Butler [2] by calculating the number of non-electrolyte molecules in the vicinity of an ion, and comparing with the number in the absence of ions. In the case of a gas or of a volatile non-electrolyte it should be possible to calculate the activity coefficient from the equilibrium at the liquid-gas interface. The activity coefficients of such solutes are obtained experimentally from their partial vapour pressures, or from their solubilities in the pure solvent and in the salt solution.

Consider first the gas or vapour in equilibrium with the pure solvent. The rate at which molecules enter the liquid is given by

$$n_1 = N_1\theta\sqrt{\frac{RT}{2\pi M}} \quad . \quad . \quad . \quad . \quad (1)$$

where N_1 is the number of gas molecules of molecular weight M per c.c., and θ is the fraction striking the surface that are not reflected (θ may be small, *cf.* Alty [3]). The rate at which dissolved molecules leave the liquid phase is given by

$$n_2 = N_2\sqrt{\frac{RT}{2\pi M}}e^{-E/RT} \quad . \quad . \quad . \quad . \quad (2)$$

where N_2 is the number of dissolved gas molecules per c.c., and E is the work done in overcoming the attractive forces of the liquid. (The attractive forces of the gas phase on a molecule entering the liquid have been neglected in comparison.) At equilibrium $n_1 = n_2$, and

$$N_2 = N_1\theta\, e^{E/RT} \quad . \quad . \quad . \quad . \quad (3)$$

Similar considerations will give the solubility (N_2') of the gas in a solution containing an electrolyte, as

$$N_2' = N_1'\theta'\, e^{E'/RT} \quad . \quad . \quad . \quad . \quad (4)$$

If two solutions at the same concentration ($N_2 = N_2'$) are compared, then the activity of the gas in the salt solution is

$$f = \frac{p'}{p} = \frac{N_1'}{N_1} = e^{(E-E')/RT} \quad . \quad . \quad . \quad (5)$$

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[1] Debye and McAulay, *Physik. Z.*, 1925, **26**, 22.

[2] Butler, *J. Physic. Chem.*, 1929, **33**, 1015.

[3] Alty, *Proc. Roy. Soc.*, *A*, 1931, **131**, 554.

If two solutions at the same partial pressure are compared ($N_1 = N_1'$) the activity coefficient is

$$f = \frac{N_2}{N_2'} = e^{(E - E')/RT} \quad . \quad . \quad . \quad . \quad (6)$$

The activity coefficient thus depends on the difference in the work done in crossing the phase boundary when pure solvent is replaced by solution. This work is electrical and depends on the number of ions present in the solution.

Consider now the electrical work done in removing a non-electrolyte molecule from its ionic environment in the liquid ; this will be equal but opposite in sign to the electrical work in building up this environment. The work done in moving an ion of charge $z_i\epsilon$ from infinity to a distance r from a molecule of polarisability α is

$$\int_{\infty}^{r} \frac{2\alpha z_i^2\epsilon^2}{D_0^2 r^5} dr = -\frac{\alpha z_i^2\epsilon^2}{2D_0^2 r^4} . \quad . \quad . \quad . \quad . \quad (7)$$

where D_0 is the dielectric constant of the solvent. The total work in forming the ionic environment up to a distance b from the molecule will be

$$-n'\int_{\infty}^{b} \frac{\alpha \Sigma z_i^2\epsilon^2}{2D_0^2 r^4} . 4\pi r^2 dr = n'\frac{4\pi\alpha\Sigma z_i^2\epsilon^2}{2D_0^2 b} . \quad . \quad . \quad . \quad (8)$$

where n' is the number of ions per c.c.

This gives the electrical work per molecule and when introduced into (5) gives

$$\log f = n'\frac{4\pi\alpha\Sigma z_i^2\epsilon^2}{2D_0^2 bkT} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The non-electrolyte molecule has displaced a solvent molecule; the polarisability α is therefore the difference between the polarisabilities of these two. Now the dielectric constant is related to the polarisability by $D = 4\pi\alpha + 1$, and hence

$$D_0 - D = 4\pi\alpha n$$

where D is the dielectric constant of the solution containing n molecules of non-electrolyte per c.c. For such solutions

$$D = D_0 (1 - an)$$

where a is a constant; hence

$$\frac{4\pi\alpha}{D_0} = \frac{D_0 - D}{D_0 n} = a \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Equation (9) now becomes

$$\log f = n'a\frac{\Sigma z_i^2\epsilon^2}{2D_0 bkT} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where b is the sum of the radii of the non-electrolyte molecule and the ion. This is identical with the equation obtained by Debye and McAulay.

Discussion and Extension of the Theory.

The validity of this relation for the solubilities of gases in salt solutions has been examined by Randall and Failey,[4] who found that the ratio log f/μ was approximately constant for several gases. The calculation of the activity coefficient requires a knowledge of the variation of the dielectric constant of the solution of the gas with its concentration, data very difficult to obtain. An approximate calculation can be made by using equation (9) combined with the Clausius-Mosotti equation,

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[4] Randall and Failey, *Chem. Rev.*, 1927, 4, 285.

$$\frac{D-1}{D+2}\cdot\frac{M}{d}=\frac{4\pi N}{3}\alpha \quad . \quad . \quad . \quad . \quad (13)$$

in which D is the dielectric constant of the medium, M its molecular weight, α its density, and N the Avogadro number. The values calculated in this way, however, for hydrogen and other gases are not in agreement with those found experimentally. Agreement with the theory is better when the activity coefficient is obtained from the vapour pressure of the volatile component of a mixture, for example for ethyl alcohol in aqueous lithium chloride solutions, but this case should be treated by the method indicated below. Agreement is obtained for aqueous solutions of solid non-electrolytes such as cane sugar.

According to the simple treatment outlined above, the salting out is attributed entirely to the change in the distortion of the non-electrolyte molecule produced by the electric field in the vicinity of an ion. The result should therefore apply only to a non-polar solute and a non-polar solvent. In the case of polar molecules the work term due to the permanent moment of both solute and solvent must be added to that previously calculated. This work may be evaluated in the following manner.

The work done in moving an ion of charge $z_i\epsilon$ from infinity to a distance r from a non-deformable non-electrolyte molecule of permanent moment μ is given by

$$\int_{\infty}^{r}\frac{2\mu z_i\epsilon}{D_0 r^3}\mathrm{d}r=\frac{\mu z_i\epsilon}{D_0 r^2} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The work done in forming the total ionic environment of the non-electrolyte molecule is then

$$n'\int_{\infty}^{b}\frac{\mu z_i\epsilon}{D_0 r^2}4\pi r^2\mathrm{d}r=\frac{4\pi n' b\mu z_i\epsilon}{D_0} \quad . \quad . \quad . \quad (15)$$

This term substituted in (6) gives the contribution of the permanent moment to the activity coefficient. As the non-electrolyte molecule displaces a solvent molecule, the expression for the activity coefficient must contain a similar term involving its permanent moment.

The total activity coefficient of the non-electrolyte is thus given by

$$\log f=n'\frac{4\pi\Sigma z_i^2\epsilon^2}{2D_0^2bkT}(\alpha_0-\alpha_1)+n'\frac{4\pi b\Sigma z_i\epsilon}{D_0kT}(\mu_0-\mu_1) \quad . \quad (16)$$

in which the subscripts $_0$ and $_1$ refer to the solvent and solute respectively. The separate distortion polarisabilities of solute and solvent may be found from the general equation for the total polarisability

$$\frac{D-1}{D+2}\cdot\frac{M}{d}=\frac{4\pi N}{3}\left(\alpha+\frac{\mu^2}{3kT}\right) \quad . \quad . \quad . \quad (17)$$

Substituting these values of α in equation (16) we obtain

$$\log f=n'\frac{4\pi\Sigma z_i^2\epsilon^2}{2D_0^2bkT}\Bigg[\frac{D_0-1}{D_0+2}\cdot\frac{M_0}{\mathrm{d}_0}\frac{3}{4\pi N}$$
$$-\frac{\mu_0^2}{3kT}-\frac{D_1-1}{D_1+2}\cdot\frac{M_1}{d_1}\cdot\frac{3}{4\pi N}+\frac{\mu_1^2}{3kT}\Bigg]+n'\frac{4\pi b\Sigma z_i\epsilon}{D_0kT}(\mu_0-\mu_1) \quad (18)$$

Further terms may be introduced into this expression to account for the contribution of the ionic atmosphere and of the interaction of dipoles to the electrical work, but in view of the uncertainty of the value of *b*, which is strictly the distance between the centres of the ion and non-electrolyte at the position of nearest approach, of the assumption that the polarisability of the solute is the same in the solution as in the pure condition and of the application of the Clausius-Mosotti expression to solutions of this type, such refinements seem hardly justifiable.

According to equation (18) log *f* should be proportional to the salt concentration, which is in accordance with the conclusions of Randall and Failey.[4] As mentioned above, in the calculation of log *f* there is some uncertainty in ascribing a value to *b*; the hydration of the ions, and possibly of the non-electrolyte molecules, will make its value rather greater than would otherwise be anticipated. The larger the value of *b* the less the first, but the greater the second term in equation (18) becomes. By choosing values of *b* of a reasonable order of magnitude, the theory may be applied to the following cases for which experimental data are available.

(*a*) *Hydrogen in Aqueous Salt Solutions.*

Here $\mu_0 = 1{\cdot}85 \times 10^{-18}$, $\mu_1 = 0$, $D_0 = 81{\cdot}2$, $D_1 = 1{\cdot}000264$, with a value of *b* of 3×10^{-8} cm., log *f* is 0·06. The experimental value of log *f* varies with the nature of the salt, but lies between 0·01 and 0·1.

(*b*) *Ethyl Alcohol in Aqueous Lithium Chloride Solutions.*

Here $\mu_0 = 1{\cdot}85 \times 10^{-18}$, $\mu_1 = 1{\cdot}7 \times 10^{-18}$, $D_0 = 81{\cdot}2$, $D_1 = 26{\cdot}8$ $d_1 = 0{\cdot}78$. With *b* as 10×10^{-8} cm., log *f* is of the order 0·033, while the experimental value calculated from the vapour pressure data of Shaw and Butler [5] and of Butler and Thomson [6] for molar salt and four moles per cent. alcohol is 0·14, and for molar salt and two moles per cent. alcohol is 0·17. In order to obtain a value of log *f* of 0·1, *b* must be taken as 60×10^{-8} cm., which is improbably high. In this case the moment for alcohol lies close to that of water, making the second term of (18) small. The moment of the dissolved alcohol may, however, have a different value, which may be evaluated approximately as follows. The polarisation of a solution is given by

$$P = \frac{D-1}{D+2} \cdot \frac{n_1M_1 + n_2M_2}{d} = n_1P_1 + n_2P_2 \quad . \quad . \quad (19)$$

where *D* is its dielectric constant, *d* its density, n_1 and n_2 the mole fractions of the components, M_1 and M_2 their molecular weights, and P_1 and P_2 the polarisations to be ascribed to each. The dielectric constant of a solution containing two moles per cent. of alcohol was taken as 78·6, the polarisation (P_2) for water calculated from its dielectric constant, and P_1 calculated from (19). The polarisability of dissolved alcohol was assumed to be the same as in the pure state, and was calculated from its refractive index, and then the moment of the dissolved alcohol obtained from

$$P_1 = \frac{4\pi N\alpha}{3} + \frac{4\pi N}{3} \cdot \frac{\mu^2}{3kT} \quad . \quad . \quad . \quad . \quad (20)$$

The value so found was $1{\cdot}4 \times 10^{-18}$, which in (18) gives log *f* as 0·1 with *b* taken as 21×10^{-8} cm.; this agrees better with the experimental result.

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[5] Shaw and Butler, *Proc. Roy. Soc.*, *A*, 1930, **129**, 519.
[6] Butler and Thomson, *ibid.*, 1933, **141**, 86.

(*c*) *Ethyl Ether in Aqueous Univalent Chloride Solutions.*

In this case $\mu_0 = 1{\cdot}85 \times 10^{-18}$, $\mu_1 = 1{\cdot}2 \times 10^{-18}$, $D_0 = 81{\cdot}2$, $D_1 = 4{\cdot}37$, $d_1 = 0{\cdot}71$. With b as 20×10^{-8} cm., $\log f$ is 0·13, while the experimental value calculated from the data of Euler [7] for molar lithium chloride is 0·18, and for molar sodium chloride is 0·22.

(*d*) *Acetone in Aqueous Salt Solutions.*

Here $\mu_0 = 1{\cdot}85 \times 10^{-18}$, $\mu_1 = 2{\cdot}7 \times 10^{-18}$, $D_0 = 81{\cdot}2$, $D_1 = 21{\cdot}5$. In this case the theory breaks down as the calculated value of $\log f$ has the wrong sign. This discrepancy is probably to be explained by the difference between the moment of acetone in solution and in the pure state. For both alcohol and ether μ is the same for the gaseous and liquid states, but this is not the case for acetone.

(*e*) *Hydrocyanic Acid in Aqueous Salt Solutions.*

Here $\mu_0 = 1{\cdot}85 \times 10^{-18}$, and $\mu_1 = 2{\cdot}6 \times 10^{-18}$. The activity coefficient should therefore be less than unity, and the solute salted in. The experimental value [9] found by distribution is 0·95 for sodium chloride, and 0·97 for lithium chloride. That calculated from (18) is 0·95.

The value of the first term in equation (18) may be calculated from refractive indices instead of dielectric constants, although this method is only approximate, as an extrapolation to infinite wave-length must be made. The polarisability is given by

$$\frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{d} = \frac{4\pi N}{3}\alpha \quad . \quad . \quad . \quad . \quad (21)$$

where n is the extrapolated refractive index. The first term calculated in this way is of the same order of magnitude as before, and results in only a very small change in $\log f$ especially if b is large. It should be observed that in all cases the major part of the effect is ascribed to the second term, which involves the permanent moment of the molecules involved.

The more Exact Theory of Salting Out.

A more exact theory of the salting out effect than that referred to above has been given by Debye [8] and by Gross,[9] who obtained an expression for the activity coefficient which is an improvement on equation (12). An account of this theory is given in Falkenhagen's *Electrolytes* (Oxford, 1934), which contains a full bibliography. The method employed is essentially thermodynamic, but a similar result may be obtained from the considerations outlined above.

According to equation (7), the work done in moving an ion of charge $z_i\epsilon$ from infinity to a distance r from a molecule of polarisability α is given by

$$\int_{\infty}^{r} \frac{2\alpha z_i^{\,2}\epsilon^2}{D_0^{\,2} r^5}\,\mathrm{d}r = -\frac{\alpha z_i^{\,2}\epsilon^2}{2D_0^{\,2} r^4}.$$

In order to calculate the activity coefficient from (6) the total electrical work in building up the ionic environment of a non-electrolyte molecule up to a distance r was obtained. This picture, however, is rather too simple as it does not take into account the change in the concentration of the non-electrolyte in the vicinity of an ion. According to (6), the activity coefficient of those non-electrolyte molecules contained in a shell of thickness dr at a distance r from a central ion is

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[7] Euler, *Z. physik. Chem.*, 1894, **31**, 360; 1904, **49**, 303.

[8] Debye, *ibid.*, 1927, **130**, 56.

[9] Gross, *Monatsh.*, 1929, **53/54**, 449; Gross and Scharz, *Wiener Sitz.*, 1930, II*b*, 139, 179; Gross and Iser, *ibid.*, 1930, II*b*, 139, 221.

$$f' = e^{\alpha z_i^2 \varepsilon^2/2D_0^2 r^4 kT} \quad . \quad . \quad . \quad . \quad (22)$$

This gives the ratio of the number of non-electrolyte molecules per unit volume in the absence of salt to the number per unit volume at a distance r from the ion. The mean number of non-electrolyte molecules round an ion will therefore be

$$\int N_2 e^{-\alpha z_i^2 \varepsilon^2/2D_0^2 r^4 kT} \mathrm{d}V \quad . \quad . \quad . \quad . \quad (23)$$

where the integration is extended over the available volume for one ion. The number of non-electrolyte molecules in the vicinity of an ion before the addition of salt is given by

$$\int N_2 \mathrm{d}V \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Consequently

$$f = \frac{N_2}{N_2'} = \frac{\int \mathrm{d}V}{\int e^{-\alpha z_i^2 \varepsilon^2/2D_0^2 r^4 kT} \mathrm{d}V} \quad . \quad . \quad . \quad (25)$$

The volume considered corresponds to a singe ion and so

$$\int \mathrm{d}V = \frac{1}{n'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

where n' is the number of ions per unit volume. Thus

$$\frac{1}{f} = n' \int e^{-\alpha z_i^2 \varepsilon^2/2D_0^2 r^4 kT} \mathrm{d}V = 1 - n' \int_b^\infty (1 - e^{-\alpha z_i^2 \varepsilon^2/2D_0^2 r^4 kT}) 4\pi r^2 \mathrm{d}V \quad (27)$$

If the salting out coefficient is defined by

$$\sigma = \int_b^\infty (1 - e^{-\alpha z_i^2 \varepsilon^2/2D_0^2 r^4 kT}) 4\pi r^2 \mathrm{d}V \quad . \quad . \quad . \quad (28)$$

then

$$N'_2 = N_2(1 - n'\sigma)$$

and

$$\frac{1}{f} = 1 - n'\sigma \quad . \quad . \quad . \quad . \quad . \quad (29)$$

The result obtained by the Debye theory gives

$$\sigma = \int_b^\infty (1 - e^{-\tilde{R}^4/r^4})\, 4\pi r^2 \mathrm{d}V \quad . \quad . \quad . \quad (30)$$

where $\tilde{R}$ is a characteristic length, which is given by

$$\tilde{R}^4 = \frac{z_i^2 \epsilon^2}{8\pi v_1 kT} \frac{1}{D_m^2} \left(v_2 \frac{\partial D_m}{\partial n_1} - v_1 \frac{\partial D_m}{\partial n_2} \right) \quad . \quad . \quad . \quad (31)$$

where n_1 and n_2 are the numbers of molecules per c.c. and v_1 and v_2 are corresponding volumes ($v_1 n_1 + v_2 n_2 = 1$ for an ideal solution).

If the dielectric constant follows a linear law

$$D_m = D_0(1 - a n_2)$$

then the characteristic length may be written

$$\tilde{R}^4 = \frac{z_i^{\,2}\epsilon^2}{8\pi kT} v_1 \frac{D_0 - D}{D_0^{\,2}} \quad . \quad . \quad . \quad . \quad . \quad (32)$$

From (11)

$$D_0 - D = 4\pi\alpha n$$

and

$$\grave{R}^4 = \frac{\alpha z_i^{\,2}\epsilon^2}{2D_0^{\,2}kT} = \frac{(E - E')r^4}{kT} \quad . \quad . \quad . \quad . \quad (33)$$

which is the value obtained by a comparison of (28) and (30).

This calculation may be regarded from a slightly different angle. If the activity coefficient of the non-electrolyte molecules contained in the shell is given by (22), then to obtain the mean activity coefficient we must integrate over the whole available volume; thus

$$f = \int e^{\alpha z_i^{\,2}\epsilon^2/2D_0^{\,2}r^4kT}\mathrm{d}V \quad . \quad . \quad . \quad . \quad . \quad (34)$$

and for a solution containing n' ions

$$f = \int_b^\infty e^{\alpha z_i^{\,2}\epsilon^2/2D_0^{\,2}r^4kT}4\pi r^2\mathrm{d}V \quad . \quad . \quad . \quad . \quad (35)$$

which leads to the same result as before.

These considerations may be applied also to the solubilities of gases in solutions containing non-electrolytes. In this case the work term in (5) is determined by the attractive forces between dissolved gas molecules and those of the added non-electrolyte. That this work is less than when ions are present is shown by the small change in solubility produced by non-electrolytes. An increased solubility will result if the attractive forces between dissolved gas and solvent molecules are greater than those between the dissolved gas and the added non-electrolyte molecules which displace the solvent. This appears to be the case for the solubility of hydrogen and nitrous oxide in aqueous solutions of chloral hydrate and for nitrous oxide in solutions of urea.

In the above treatment the possible effect of a potential at the phase interface has been omitted. The parallelism between this potential and the salting out order of anions suggests that there may be a connection between the two. This point, however, is one which requires further investigation.

Summary.

The activity coefficient of a non-electrolyte is derived from considerations of the equilibrium between the liquid and the vapour phases, and is shown to be given by $e^{E/RT}$, where E is the electrical work involved in the passage of ions from one phase to the other. This work is calculated from the change in polarisability of the non-electrolyte molecule and the equation of Debye and McAulay is obtained. A more complex expression for the activity coefficient is derived including the permanent moment of the non-electrolyte molecule and its application to cases for which experimental data are available is discussed. It is also shown that the salting-out equation of Debye and Gross may be obtained from similar considerations.

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ION EQUILIBRIUM IN HEAVY WATER.[*]

By C. Drucker.

Received 15*th February*, 1937.

An investigation had been started in this Institute to decide how far the stability limits of proteins are changed if heavy water, instead of ordinary water, is used as the solvent of the solutions examined in the ultracentrifuge.[1] Following a suggestion of Professor Svedberg it was sought to determine the difference, if any, in the acidity of buffer solutions prepared with heavy and ordinary water and, in this connection, the behaviour of hydrogen electrodes in D_2O was examined in a more general way.

Before potential measurements can give information as to the acidity of a substance dissolved in D_2O we must know the solution tension of D_2 in relation to the standard H_2 electrode in H_2O as zero, and if, in addition, solutions in D_2O and in H_2O are in mutual contact, the diffusion potential arising at the interface should be known.

The latter problem does not seem, at present, to be soluble either theoretically or experimentally. It seems legitimate, however, in this particular case, to neglect it. The interpretation of the following results is made on the explicit assumption that the diffusion potential between a solution in H_2O and a solution in D_2O (or in a mixture of the two) is—within 1 mV—equal to the diffusion potential between the same solutions in H_2O.

Before the main measurements were made, the behaviour of the D_2 electrode in different solutions has been studied.

Experimental Procedure.

Pipette micro-electrodes [2] supplied with thin platinized platinum wires were used,[†] one for H_2 and one for D_2. Each contained about 0·05 c.c.; the total amount required for each measurement was roughly 0·15 c.c. The electrodes (connected to the gas tanks by glass tubing supplied with the necessary stopcocks and ground joints without intervening rubber tubing) dipped into small beakers blown directly from capillaries. The counter-electrode was connected in the usual way to the other end of the capillary, if necessary by way of an interposed agar salt bridge. When a few c.c. of gas had been passed through the solution it was sucked back. The arrangement allowed immediate readings and convenient renewal. The error of the readings was below 0·1 mV. except in a few cases of high resistance where it might reach 0·5 mV. Having regard to diffusion potentials the experimental error may be taken as 1 mV.

The solutions were prepared in small amounts varying between 0·5 and 1 c.c. The concentrations are given in mols./litre; the weighing errors were about 1 per cent. in general and up to 5 per cent. in a few exceptional cases.

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[*] This paper was ready for publication already in March, 1936. Circumstances over which the author had no control have delayed it for about ten months.

[1] The Svedberg and J. B. Eriksson-Quensel, *Nature*, 1936, **137**, 400.

[2] Ostwald-Luther, *Hand u. Hülfsbuch*, 5 Aufl. Fig. 428.

[†] Glass electrodes have been used by some authors, but it has not been proved that they act as reversible electrodes for the equilibrium $D_2+2H' \rightleftharpoons H_2+2D'$.

Both kinds of hydrogen were prepared, in micro-gas generators, from water made slightly alkaline by sodium hydroxide and aluminium. In some cases sodium was used with no difference in the results. Before filling, the generator and the attached gas burette were evacuated to 0·1 mm. Hg by a mercury Boltwood pump. As very little oxygen was left in the gas the electrodes attained equilibrium rapidly.

The Combination Pt/H_2, Solution/D_2/Pt.

This cell can only give a definite potential if at least one of the electrodes is changed in such a way that the ratios of solution tensions to ionic activities are the same. If, for instance, the solution is prepared with H_2O—analogous considerations apply, of course, to D_2O—then the reaction $D_2 + 2H^+ = H_2 + 2D^+$ is bound to proceed, on the D_2 side, until the ionic activities there existing are linked to the partial pressures P_D of D_2 ond P_H of H_2 by the equation

$$\frac{P_H}{[H^\cdot]^2} = \frac{P_D}{[D^\cdot]^2}. \quad . \quad . \quad . \quad . \quad (1)\,*$$

If this condition is fulfilled, the total potential of the cell, E, is the sum of the three potentials E_H (on the unchanged H_2 side), E_D (on the D_2 side where the reaction outlined above has brought about changes) and a third potential E_m (which may or may not differ from zero), because on the D_2 side two different solutions are in contact with each other. The difference of composition, however, is bound to be soon eliminated by diffusion. Since, in addition the mass of the solution greatly exceeds the mass of the gas phase, the changes in solution are but small. We shall assume, therefore, that E_m can be neglected. In this case $E = E_D - E_H$.

A number of cells of this character were examined, some, (A), simple combinations as indicated, others, (B), with a calomel electrode interposed as an auxiliary electrode, that is to say the difference was measured by means of the cells

$$\left.\begin{array}{l} \overset{-}{\text{Pt}}/\text{H}_2,\ \text{solution/KCl, HgCl/}\overset{+}{\text{Hg}} \\ \overset{-}{\text{Pt}}/\text{D}_2,\ \text{solution/KCl, HgCl/}\overset{+}{\text{Hg}} \end{array}\right\} \quad . \quad . \quad . \quad (B)$$

Table I. records, in millivolts, the potential differences ϵ_A and ϵ_B found according to schedules A and B under identical conditions of 18° and 760 mm. pressure. In column L the electrolyte used and its p_H in H_2O solution is specified, r is the percentage by weight of D_2O in the solvent. A plus sign denotes that positive current passes from D_2 to H_2.

It is seen that in every case the potential of the changed electrode is not only accurately

TABLE I.

r.	L.	ϵ_A.	ϵ_B.
5·8	Acetate buffer $p_H = 4·1$	+2	—
14·6	,, ,, ,,	−1	0
44·0	,, ,, ,,	−2	−1
81·4	,, ,, ,,	+1	+1
92·5	,, ,, ,,	−1	−1
18·3	Phosphate buffer $p_H = 6·4$	0	0
99·6	Sulphuric acid 0·068 mol.	0	−1
0	,, ,, ,,	0	+1
68·5	Acetic acid 0·066 mol.	0	—
89	Hydrochloric acid 0·092 mol.	—	0

---

* As HD is formed during the process, the corresponding relation is valid for this component.

defined [3] but is also equal to the potential of the other electrode, whether or not the latter has changed and whether or not equilibrium between the solution and the gas phase as a bulk has taken place. Therefore, the equation holds true

$$58 (\log \sqrt{P_D} - \log [D^\cdot]) = 58 (\log \sqrt{P_H} - [H^\cdot]) . \qquad (1a)$$

Supposing that the potential values are not affected by any diffusion potential they can be used to calculate the ratio of the two partial pressures and the solution tension of D_2, if the ionic activities are known.

In connection with these experiments the following cells have been measured [4] at 760 mm. at t° :—

$\overset{-}{Pt}/D_2, \underset{c = 0{\cdot}068}{D_2SO_4}, Hg_2SO_4/\overset{+}{Hg}$ in D_2O 99·6 per cent. $\epsilon_5 = 756{\cdot}0$ (18°)

$\overset{-}{Pt}/H_2, \underset{c = 0{\cdot}068}{D_2So_4}, Hg_2SO_4/\overset{+}{Hg}$ in D_2O 99·6 per cent. $\epsilon_{12} = 756{\cdot}6$ (18°)

$\overset{-}{Pt}/H_2, \underset{c = 0{\cdot}068}{H_2SO_4}, Hg_2SO_4/\overset{+}{Hg}$ in H_2O $\epsilon_1 = 746{\cdot}2$ (18°)

$\overset{-}{Pt}/D_2, \underset{c = 0{\cdot}068}{H_2SO_4}, Hg_2SO_4/\overset{+}{Hg}$ in H_2O $\epsilon_{11} = 745{\cdot}7$ (18°)

$\overset{-}{Pt}/D_2, \underset{0{\cdot}092}{DCl}, AgCl/\overset{+}{Ag}$ in D_2O 89 per cent. $\epsilon_{20} = 351{\cdot}8$ (20°)

$\overset{-}{Pt}/H_2, \underset{0{\cdot}092}{HCl}, AgCl/\overset{+}{Ag}$ in D_2O 89 per cent. $\epsilon_{24} = 352{\cdot}0$ (20°)

Even here final readings were quickly obtained. As the right-hand electrodes for every solvent are identical it follows that the corresponding hydrogen electrodes must have the same potentials whether started with D_2 or H_2.

Consequently, since in mixtures of D_2O and H_2O the potential is defined by D_2 and $D^\cdot$ and by H_2 and $H^\cdot$ simultaneously and since the ratio of the partial pressures is determined by the composition of the solvent, both the values of $[D^\cdot]$ and $[H^\cdot]$ in solution can be found.

The Solution Tension of Heavy Hydrogen.

Suppose a solution in pure D_2O to be measured against the standard calomel electrode. The activities $[D^\cdot]$ and $[H^\cdot]$ can be calculated for solutions of deuteroacetic acid in D_2O, both in the absence and in the presence of sodium acetate, from the dissociation constant $k_2 = 0{\cdot}59 \times 10^{-5}$ found by Lewis and Schutz [5] by means of conductivity measurements. We are using this value though the correct one is possibly a few per cent. lower.

The following combinations were measured :

(*a*) $\overset{-}{Pt}/D_2$, buffer solution in $D_2O/\underset{2{\cdot}0}{KCl}/\underset{1{\cdot}0}{KCl}, HgCl/\overset{+}{Hg}$

(*b*) $\overset{-}{Pt}/H_2$, buffer solution in $H_2O/\underset{2{\cdot}0}{KCl}/\underset{1{\cdot}0}{KCl}, HgCl/\overset{+}{Hg}$

---

[3] Buffer solutions in pure D_2O in contact with H_2, and solutions in pure H_2O in contact with D_2O gave initial readings of a few millivolts, due presumably to the absence of one component.

[4] D_2SO_4 and DCl means that the solutions were prepared with HCl and H_2SO_4 in heavy water.

[5] Lewis and Schutz, *J. Am. Chem. Soc.*, 1934, 56, 1002, 1913.

the (*b*) cells were employed for the sake of comparison, and the solutions were prepared in minute amounts. The KCl solutions were made with H_2O. For the measurements in Table II.(A) a 98 per cent. preparation of D_2O was used, for those in Table II.(B) a still purer sample of 99·6 per cent. was available. *t* and *B* denote temperature and barometric pressure, p_H the acidity in H_2O as calculated or taken from tables. ϵ_D and ϵ_H are the readings of e.m.f., ϵ_H' is calculated from ϵ_H by reduction to the concentration of the corresponding D_2O solution. D denotes an experiment made according to the *a*-arrangement, H one made according to *b*.

The difference $\Delta_\epsilon = \epsilon_D - \epsilon_H'$ in Part A is practically the same for all solutions averaging 27 millivolts. The results of the second series are almost identical.

TABLE II.

Exp.	Solution.		*t*.	*B*.	p_H.	ϵ_D.	ϵ_H.	ϵ_H'.	Δ_ϵ.
Part A.									
D 1	HAc NaAc	0·105 0·105	17·0	757	—	574	—	—	—
H 1	HAc NaAc	0·103 0·097	16·6	748	4·6	—	548	549	25
D 2	HAc NaAc NaCl	0·485 0·037 1 %	18·0	756	—	508	—	—	—
H 13	HAc NaAc NaCl	0·465 0·038 1 %	17·0	738	4·8	—	484	482	26
D 5	HAc NaAc	0·114 0·097	19·0	758	—	575	—	547*	28
D 6	Na_2HPO_4 KH_2PO_4	0·021 0·139	18·6	775	—	652	—	—	—
H 3	Na_2HPO_4 KH_2PO_4	0·021 0·141	18·7	772	5·9	—	626	626	26
D 7	Na_2HPO_4 KH_2PO_4	0·130 0·055	18·3	762	—	716	—	—	—
H 4	Na_2HPO_4 KH_2PO_4	0·130 0·056	18·3	762	7·0	—	687	688	28
D 8	Na_2HPO_4 KH_2PO_4	0·174 0·009	18·0	762	—	763	—	—	—
H 5	Na_2HPO_4 KH_2PO_4	0·173 0·010	17·5	768	7·9	—	736	737	26
D 9	Na_2HPO_4 KH_2PO_4	0·034 0·034	18·0	762	—	702	—	—	—
H 6	Na_2HPO_4 KH_2PO_4	0·036 0·035	18·1	762	6·8	—	676	676	26
D 10	Na_2CO_3 $Na_2B_4O_7$	0·022 0·046	18·8	768	—	850	—	—	—
H 12	Na_2CO_3 $Na_2B_4O_7$	0·021 0·046	16·2	747	9·2	—	823	823	27
D 12	Na_2CO_3 $Na_2B_4O_7$	0·053 0·0109	17·0	767	—	899	—	—	—
H 10	Na_2CO_3 $Na_2B_4O_7$	0·054 0·0109	18·0	773	10·2	—	867	867	32

* Calculated from concentration.

TABLE II—*continued.*

Exp.	Solution		t.	B.	p_H.	ϵ_D.	ϵ_H.	ϵ_H'.	Δ_ϵ.
Part B.									
D 13	HAc	0·168	17·2	753	—	522	—	—	—
	NaAc	0·0140							
H 14	HAc	0·187	18·4	749	3·6	—	493	493	29
	NaAc	0·0156							
D 15	HAc	0·062	17·2	748	—	602	—	—	—
	NaAc	0·140							
H 15	HAc	0·077	17·4	751	4·9	—	565	571	31
	NaAc	0·140							
D 15	Na_2HPO_4	0·020	17·0	753	—	689	—	—	—
	KH_2PO_4	0·041							
H 16	Na_2HPO_4	0·020	17·4	754	6·4	—	655	655	34
	KH_2PO_4	0·041							
D 16	Na_2HPO_4	0·054	16·3	773	—	736	—	—	—
	KH_2PO_4	0·0136							
H 17	Na_2HPO_4	0·056	17·5	755	7·4	—	706	705	31
	KH_2PO_4	0·0140							
D 17	Na_2CO_3	0·023	16·0	785	—	858	—	—	—
	$Na_2B_4O_7$	0·027							
H 18	Na_2CO_3	0·023	17·3	758	9·5	—	829	830	28
	$Na_2B_4O_7$	0·027							
D 18	Na_2CO_3	0·044	16·0	782	—	918	—	—	—
	$Na_2B_4O_7$	0·0052							
H 20	Na_2CO_3	0·042	17·6	753	10·5	—	884	886	32
	$Na_2B_4O_7$	0·0048							
D 20	HAc	0·107	17·6	770	—	465	—	450*	15

* Calculated from concentration.

Here the average of $\Delta\epsilon$ is 30 millivolts, which occurs to be slightly higher than in II.A. The difference is probably real, partially at least. The ratio of the dissociation constants of the two acetic acids $k_1 : k_2 = 1·86 : 0·59 = 3·16$ which is also the ratio of the activities of $H^\cdot$ and $D^\cdot$, since the concentrations of anion and of undissociated acid are the same in both solvents. The potential difference between the two gas half-cells is therefore

$$\Delta\epsilon = \epsilon_D - \epsilon_H' = 58 (\log \sqrt{P_D} - \log \sqrt{P_H} - \log [D^\cdot] + \log [H^\cdot])$$

or

$$30 - 58 \log 3·16 = 58 (\log \sqrt{P_D} - \log \sqrt{P_H}) = 1 \text{ mV}.$$

One millivolt lies within the errors of observation, so that *the solution tensions of* D_2 *and* H_2 *are equal.*

Experiment D20 (series II.B) carried out with acetic acid in absence of neutral salt gives the same result as the buffers. Here we have

$$[H^\cdot]^2 : [D^\cdot]^2 = k_1 : k_2$$

therefore

$$15 - 58 \log \sqrt{3·16} = 0.$$

Abel, Bratu and Redlich [6] measured the e.m.f. of the following cell

$$\overset{+}{Pt}/D_2, \underset{0·1}{DCl}, AgCl/Ag/AgCl, \underset{0·1}{HCl}, H_2/\overset{-}{Pt}$$

---

[6] Abel, Bratu and Redlich, *Z. physik. Chem.*, *A*, 1935, 173, 353.

at 21°, the pressure on each side being 1 atm. They found 3·4 mV. which they accepted as the normal potential of D_2 in relation to a solution in D_2O, if H_2 over H_2O solution gives zero. Determining the potential difference of the two AgCl half-cells, one can calculate from the value 3·4 mV. found for the double cell, the actual difference existing between the two gas half-cells. The cell

$$\overset{-}{\text{Hg}}/\text{HgCl, KCl in } D_2O/\text{KCl in } H_2O, \text{ HgCl}/\overset{+}{\text{Hg}}$$

with normal solutions on both sides was found to have $\epsilon_9 = 3{\cdot}5$ mV. at 18°. If we neglect the diffusion potential and if the following activity relations are valid,

$$\left[\frac{\text{KCl } 1{\cdot}0 \text{ in } H_2O}{\text{KCl } 1{\cdot}0 \text{ in } D_2O}\right] = \left[\frac{\text{HCl } 0{\cdot}1 \text{ in } H_2O}{\text{HCl } 0{\cdot}1 \text{ in } D_2O}\right] \text{ and } \left[\frac{\text{HgCl in } H_2O}{\text{HgCl in } D_2O}\right] = \left[\frac{\text{AgCl in } H_2O}{\text{AgCl in } D_2O}\right]$$

then the measurements of these authors give zero as the potential difference of the two gas half-cells. Maybe the second assumption is not very safe. To verify it the following cells were measured at 18°.

$$\overset{+}{\text{Ag}}/\text{AgCl}, \underset{0{\cdot}092}{\text{DCl}} \text{ in } D_2O \text{ 89 per cent.}/X/\underset{1{\cdot}0}{\text{KCl}} \text{ in } H_2O, \text{ HgCl}/\overset{-}{\text{Hg}} \qquad \epsilon_{21}$$

$$\overset{+}{\text{Ag}}/\text{AgCl}, \underset{0{\cdot}094}{\text{HCl}} \text{ in } H_2O/X/\underset{1{\cdot}0}{\text{KCl}} \text{ in } H_2O, \text{ HgCl}/\overset{-}{\text{Hg}} \qquad \epsilon_{23}$$

(That the D_2O used was not free from H_2O is of little influence.) With X = half sat. KCl the values were $\epsilon_{21} = 2{\cdot}4$, $\epsilon_{23} = 5{\cdot}3$, with X = sat. KCl solution $\epsilon_{21} = 3{\cdot}9$, $\epsilon_{23} = 7{\cdot}3$. Extrapolation according to Bjerrum and reduction for the small difference of concentrations yields $\epsilon_{23} - \epsilon_{21} = 3{\cdot}3$ mV. The error being certainly less than 1 mV. it follows again that the solution tension of D_2 equals that of H_2. (Incidentally, the solubility ratio of AgCl in H_2O and in 89 per cent. D_2O is 1·14.)

Mixtures of D_2O and H_2O as Solvents.

Accepting equation 1*a* as established we make the further assumption, justified by facts that will be set forth below, that the equilibrium of all components in solution is, in every case, instantaneously attained and that the measured potential corresponds to the right partial pressures. The equilibrium of the water and hydrogen isotopes is known to be governed at 20° by the relations [7]

$$K_4' = \frac{[D_2O] \, . \, [H_2]}{[H_2O] \, . \, [D_2]} = 9{\cdot}2 \quad . \quad . \quad . \quad . \quad (2a)$$

$$K_5' = \frac{[HDO]^2}{[H_2O] \, . \, [D_2O]} = 3{\cdot}26. \quad . \quad . \quad . \quad (2b)$$

In 2(*a*), $[H_2]$ and $[D_2]$ which are identical with the respective partial pressures P_H and P_D can be substituted by the ion activities according to 1(*a*). These again are fixed by the buffer concentrations. For acetate buffer, where both dissociation constants are known, the activities can be computed; denoting by C the sum of the concentrations of the two isotopic acids in equilibrium, by S_H the concentration of CH_3COOH and by S_D the concentration of CH_3COOD, by a the concentration of the common anion CH_3COO', which is determined in the presence of neutral salt by the activity of the salt and in the absence of salt equals $[H^\cdot] + [D^\cdot]$. The equilibrium is then

$$\frac{S_H^2 \, . \, [D_2O]}{S_D^2 \, . \, [H_2O]} = \kappa. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

---

[7] L. and A. Farkas, *Trans. Faraday Soc.*, 1934, **30**, 1076.

In the presence of small amounts of electrolytes, $[D_2O]$ and $[H_2O]$ are the same as in the pure solvent. (The assumption made here and in the following calculations that the " dissociating power " is equal for H_2O, D_2O and their mixtures is justified by the fact that the dielectric constants are practically identical.) It follows

$$\frac{S_H}{S_D} = \frac{[H^\cdot]}{[D]} \cdot \frac{k_2}{k_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$k_1 = \frac{[H^\cdot]}{S_H} \cdot a, \quad k_2 = \frac{[D^\cdot]}{S_D} \cdot a \quad . \quad . \quad . \quad (4a)$$

$$K_4' \frac{[H_2O]}{[D_2O]} = \frac{[H^\cdot]^2}{[D^\cdot]^2} = \frac{S_H^2}{S_D^2} \cdot \frac{k_1^2}{k_2^2} = \frac{k_1^2}{k_2^2} \cdot \frac{[H_2O]}{[D_2O]} \cdot \kappa \quad . \quad . \quad (5)$$

$$\kappa = K_4' \cdot \frac{k_2^2}{k_1^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

For acetic acid $\kappa = 9{\cdot}2 \times (0{\cdot}316)^2 = 0{\cdot}92$. Further, according to (3)

$$\left.\begin{aligned} S_D &= \frac{C}{1 + S_H/S_D} = \frac{C}{1 + \sqrt{\kappa \frac{[H_2O]}{[D_2O]}}} \\ S_H &= \frac{C}{1 + S_D/S_H} = \frac{C}{1 + \sqrt{\frac{1}{\kappa} \cdot \frac{[D_2O]}{[H_2O]}}} \end{aligned}\right\} \quad . \quad . \quad (7)$$

which allows the calculation of S_H and S_D, and subsequently $[H^\cdot]$ and $[D^\cdot]$ by means of (4).

The partial pressures P_H and P_D can even be taken directly from the Farkas table by interpolation for the ratio r in each preparation. Then $[H^\cdot]$ and $[D^\cdot]$ can be calculated from the measured potentials. Both methods are used in the following and the results are compared.

An acetate buffer was used of p_H about 4·1, dissolved in water containing r per cent. per weight of D_2O. As stated above (Table I.) the potentials of the combinations Pt/D_2, solution, H_2/Pt made up with these solutions are zero. In the same table differences are recorded which are derived from the separate measurements of the cells B (p. 661) which gave, as pointed out, the same values for D_2—as well as for H_2—electrode. These individual values are recorded under ϵ in the following Table III.

TABLE III.

r.	HAc.	NaAc.	p_H.	t.	B.	ϵ.	ϵ'.	$\epsilon - \epsilon'$.
5·8	0·151	0·044	4·11	18·0	746	522	521	1
14·6	0·160	0·045	4·09	18·2	742	524	520	4
44·0	0·155	0·045	4·10	18·7	744	529	521	8
81·4	0·160	0·045	4·09	18·0	752	538	520	18
92·5	0·152	0·044	4·11	18·5	744	543	521	22
68·5	0·071	0	2·94	18·8	762	463	453	12

ϵ' is calculated for the H_2 electrode in H_2O solution with the equation $\epsilon' = 57{\cdot}7\, p_H + 284$.

The values of isotope concentrations and partial pressures, found by interpolation as mentioned and used in ensuing calculations are tabulated in Table IV.

TABLE IV.

r.	D_2O.	H_2O.	HDO.	D_2.	H_2.	HD.
5·8	0·4	88·7	10·9	0·047	96·6	3·4
14·6	2·3	74·4	23·3	0·30	91·2	8·5
44·0	19·0	34·2	46·3	4·0	65·6	30·4
68·5	47·5	12·0	40·5	18·5	37·2	44·3
81·4	66·5	4·0	29·4	35·0	19·0	46·0
92·5	85·3	0·7	14·0	59·3	4·8	35·0

From these figures which are, of course, not very accurate for the highest and lowest values of r, the ionic activities are calculated by

$$\log \frac{1}{[H^{\bullet}]} = \frac{\epsilon - 284}{57{\cdot}7} - \log \sqrt{[H_2]},$$

$$\log \frac{1}{[D^{\bullet}]} = \frac{\epsilon - 284}{57{\cdot}7} - \log \sqrt{[D_2]}.$$

Table V. records the results. S is the sum of $[H^{\bullet}]$ and $[D^{\bullet}]$ as found from e.f.m. p_S is $- \log S$. $[H^{\bullet}]$ and $[D^{\bullet}]$ are ion activities found by equations (7) and (4*a*) independently from potential measurements. The agreement is perfect within the experimental and calculative errors.

TABLE V.

r.	S_H	S_D.	$[H^{\bullet}]$.	$[D^{\bullet}]$.	$[H^{\bullet}]'$.	$[D^{\bullet}]'$.	S.	p_S.
5·8	0·141	0·010	$7{\cdot}4 \,.\, 10^{-5}$	$0{\cdot}16 \,.\, 10^{-5}$	$7{\cdot}6 \,.\, 10^{-5}$	$0{\cdot}17 \,.\, 10^{-5}$	$7{\cdot}6 \,.\, 10^{-5}$	4·12
14·6	0·135	0·025	6·4 ,,	0·38 ,,	7·0 ,,	0·41 ,,	6·8 ,,	4·17
44·0	0·087	0·068	4·7 ,,	1·1 ,,	4·5 ,,	1·1 ,,	5·8 ,,	4·24
81·4	0·030	0·129	1·8 ,,	2·3 ,,	1·6 ,,	2·1 ,,	4·1 ,,	4·43
92·5	0·012	0·140	0·7 ,,	2·5 ,,	0·65 ,,	2·4 ,,	3·2 ,,	4·49
68·5	0·023	0·048	$0{\cdot}48 \,.\, 10^{-3}$	$0{\cdot}34 \,.\, 10^{-3}$	$0{\cdot}51 \,.\, 10^{-3}$	$0{\cdot}34 \,.\, 10^{-3}$	$0{\cdot}85 \,.\, 10^{-3}$	3·09

In the light of these results, *the acidities of acetate buffers of different compositions in mixtures of* D_2O *and* H_2O *can be calculated without resort to electrical measurements.* The same is expected to be true for other buffers provided that the dissociation equilibria are known. It is seen from Tables II.A and II.B that phosphate buffers, possibly even borate buffers, show the same differences between D_2O and H_2O solutions as acetate buffers. The ratio of dissociation constants, therefore, seems to be in all three cases approximately 3.

The Dissociation Constants of the Water Isotopes.

The very fact that the dissociation equilibrium always exists in ordinary water justifies the assumption that the same holds true for D_2O and for mixtures of D_2O with H_2O. This conjecture is further supported by the fact that the four constants for mixtures are of similar magnitude. We put

$$\rho_1 = \frac{[H^{\bullet}] \,.\, [OH']}{[H_2O]}, \quad \rho_2 = \frac{[D^{\bullet}] \,.\, [OD']}{[D_2O]}, \quad \rho_3 = \frac{[H^{\bullet}] \,.\, [OD']}{[HDO]}, \quad \rho_4 = \frac{[D^{\bullet}] \,.\, [OH']}{[HDO]}. \quad (8)$$

From $\rho_1 = 0{\cdot}80 \, . \, 10^{-14}$ and $\rho_2 = 0{\cdot}13 \, . \, 10^{-14}$ (found by Abel and colleagues) * we get by means of equations 2(*a*) and 2(*b*)

$$\frac{\rho_1 \cdot \rho_2}{\rho_3 \cdot \rho_4} = K_2', \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9)$$

$$\frac{\rho_1 \cdot \rho_3}{\rho_2 \cdot \rho_4} = K_4', \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10)$$

with the results $\rho_3 = 0{\cdot}21 \, . \, 10^{-14}$ and $\rho_4 = 0{\cdot}15 \, . \, 10^{-14}$.

When all ions are in equilibrium one is bound to believe the molecules are too. The constants K_2' and K_4' used in our calculations have been established by means of catalytically reached equilibrium. *This catalytic effect seems to be confined to the gas phase. In solution, full equilibrium is attained at the very moment of mixing.* If, therefore, a platinised electrode, moderately fraught with D_2 or H_2, is immersed in an oxygen-free solution containing both D_2O and H_2O then the slight exchange necessary for establishing the equilibrium of electrical potentials may be expected to take place very quickly on the surface of the electrode. The readings will then be true from the very beginning.

This behaviour resembles that of platinum in a ferric-ferrous solution. There is, however, the difference that in the latter case it is the *absolute value* of the partial pressures that attains a definite level, while in the case of mixed water isotopes the *ratio* of partial pressures is fixed.

Sulphate Cells.

Hydrochloric acid is known to be a very strong electrolyte even in D_2O, *viz.*, completely dissociated just as in H_2O. G. N. Lewis and Schutz [5] were the first to conjecture, and Abel Bratu and Redlich [6] agreed, that the difference of dissociation constants of acids dissolved in the water isotopes is the greater the lower the absolute value. It was therefore regarded useful to measure the inorganic acids of intermediate strength DSO_4' and HSO_4'. At 18° and 760 mm. the following results were found :

$\overset{-}{\text{Pt}}/D_2$, $\underset{0\cdot115}{KDSO_4}$, $Hg_2SO_4/\overset{+}{\text{Hg}}$ in D_2O 99·6 per cent. $\qquad \epsilon_{14} = 762{\cdot}7$.

$\overset{-}{\text{Pt}}/D_2$, $\underset{0\cdot115}{KDSO_4}/\underset{2\cdot0}{KCl}/\underset{1\cdot0}{KCl}$, $HgCl/\overset{+}{\text{Hg}}$ in D_2O 99·6 per cent. $\qquad \epsilon_{15} = 368{\cdot}4$.

$\overset{+}{\text{Hg}}/Hg_2SO_4$, $\underset{0\cdot115}{KDSO_4}/\underset{2\cdot0}{KCl}/\underset{1\cdot0}{KCl}$, $HgCl/\overset{-}{\text{Hg}}$ in D_2O 99·6 per cent. $\qquad \epsilon_{16} = 393{\cdot}9$.

The analogous cells with H_2O gave respectively

$$\epsilon_{17} = 752{\cdot}7 \qquad \epsilon_{18} = 364{\cdot}8 \qquad \epsilon_{19} = 388{\cdot}7.$$

The difference between the two cells without transference is $\epsilon_{14} - \epsilon_{17} = 10{\cdot}0$ mV., this is almost the same as found between the sulphuric acid combinations, and much more than that found for hydrochloric acid. The difference of the hydrosulphate half-cells $\epsilon_{16} - \epsilon_{19} = +\,5{\cdot}2$ differs from that of the hydrochloric cells $-\,3{\cdot}3$. This is due, partly at least, to the fact that the dissociation of the hydrosulphate ion is very incomplete. From ϵ_9, ϵ_{15} and ϵ_{18}, we can calculate the constants, assuming that, to a sufficient approximation, the dissociation into $K^{\cdot}$ and primary anion is complete and that the classical equations are valid. One finds

$$[D^{\cdot}] = 0{\cdot}030 \qquad [H^{\cdot}] = 0{\cdot}040$$

$$\frac{[H^{\cdot}]^2}{0{\cdot}115 - [H^{\cdot}]} = 0{\cdot}021 \quad \text{for} \quad HSO_4' \rightleftharpoons H^{\cdot} + SO_4'',$$

$$\frac{[D^{\cdot}]^2}{0{\cdot}115 - [D^{\cdot}]} = 0{\cdot}010 \quad \text{for} \quad DSO_4' \rightleftharpoons D^{\cdot} + SO_4''.$$

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* This value has since been confirmed by Wynne-Jones (*Trans. Far. Soc.* 1936, **32**, 139).

The correct constant in the first [8] case is 0·017, the ratio of the two constants is 2·0 which compares * with 2·7 for monochloracetic acid and 3·1 for acetic acid according to Lewis and Schutz.[5]

The Total Dissociation of Water Mixtures Free from Electrolytes.

From the four constants calculated by equations (8), the ion concentrations of pure water mixtures can be deduced. We have

$$[H^{\bullet}] + [D^{\bullet}] = [OH'] + [OD'] \quad . \quad . \quad . \quad (11)$$

and by means of equations (2*a*) and (2*b*) one gets

$$[H^{\bullet}]^2 = \frac{\rho_1[H_2O] + \rho_3[HDO]}{1 + \frac{\rho_4}{\rho_1} \cdot \frac{[HDO]}{[H_2O]}} = \frac{\rho_1[H_2O] + \rho_3[HDO]}{1 + \sqrt{\frac{[D_2O]}{K_4' \, . \, [H_2O]}}}, \quad . \quad (12a)$$

$$[D^{\bullet}]^2 = \frac{\rho_2[D_2O] + \rho_4[HDO]}{1 + \frac{\rho_3}{\rho_2} \cdot \frac{[HDO]}{[D_2O]}} = \frac{\rho_2[D_2O] + \rho_4[HDO]}{1 + \sqrt{K_4' \frac{[HDO]}{[D_2O]}}}, \quad . \quad (12b)$$

$$[H^{\bullet}] + [D^{\bullet}] = \sqrt{\rho_1[H_2O] + \rho_2[D_2O] + (\rho_3 + \rho_4)[HDO]}. \quad . \quad (12c)$$

A table similar to Table IV. was arranged recording the proportions of the three water isotopes and Table VI. was deduced from it.

TABLE VI.

r.	[H•]. × 10⁷.	[D•]. × 10⁷.	*S*. × 10⁷.	*ξ*.
0	0·89	0·0	0·89	1·00
10	0·82	0·03	0·85	0·95
20	0·74	0·06	0·80	0·90
30	0·66	0·09	0·75	0·84
40	0·58	0·12	0·70	0·79
50	0·51	0·16	0·67	0·75
60	0·42	0·19	0·61	0·68
70	0·31	0·22	0·53	0·61
80	0·22	0·26	0·48	0·54
90	0·11	0·31	0·42	0·47
100	0·0	0·36	0·36	0·40

ξ, the sum *S* divided by the value $[H^{\bullet}] = 0{\cdot}89 \times 10^{-7}$ changes with *r* in much the same way as the velocity of mutarotation of glycose changes according to experiments made by Moelwyn-Hughes, Bonhöffer and Klar.[9] With small corrections to account for the difference of velocity in pure H_2O and pure D_2O, the two curves become identical within the experimental and calculative errors.

The explanation offering itself at first sight that the mutarotation velocity is primarily governed by the concentration of the hydroxyl ions or the hydrogen ions is contradicted by the findings of Nelson and Beegle,[10] still more by those of Brønsted and Guggenheim [11] who found the catalysis by the ions of neutral water to be negligible in comparison with the non-catalytic reaction. Moreover, Hammill and La Mer,[12] experimenting with 10^{-5} *N* hydrochloric acid found a relation of the velocity constants to *r* almost identical with the relation found in neutral water by Moelwyn-Hughes and colleagues, though in their solutions the concentration $[H^{\bullet}] + [D^{\bullet}]$ was constant 10^{-5} and that of hydroxyl ions 10^{-9}. These facts seem to rule out the possibility of a primary catalysis by the ions of water. Yet the empirical relation between ξ and r proves an indirect link to exist between the changes of reaction velocity governed by the proportions of the three isotopes and the ionic concentrations found by the equations (12*a*) and (12*b*).

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[8] C. Drucker, *Z. Elektrochemie*, 1911, **17**, 398.

* For picric acid, however, one deduces the ratio 4·0 of the two dissociation constants from partition measurements made by Gross and Wischin (*Trans. Far. Soc.*, 1936, **32**, 879). Foi other acids see Schwarzenbach, Epprecht and Erlenmeyer (*Helv. Chim. Acta*, 1936, **6**, 1292).

[9] E. A. Moelwyn-Hughes, R. Klar, and K. F. Bonhöffer, *Z. physik. Chemie*, *A*, 1934, **169**, 113.

[10] Nelson and Beegle, *J. Am. Chem. Soc.*, 1919, **41**, 559.

[11] Brønsted and Guggenheim, *ibid.*, 1927, **49**, 2554.

[12] Hammill and La Mer, *J. Chem. Physics*, 1934, **2**, 891.

Summary.

1. The solution tension of D_2 was established, by measurements, to be equal to the solution tension of H_2 and evidence is given that in liquid mixtures of D_2O and H_2O equilibrium is always in existence.
2. The ionic activities in D_2O and in mixtures of D_2O and H_2O were measured electrometrically, and it was shown that they can be calculated from the composition of the solvent.
3. The concentrations of the four ions $H^\cdot$, $D^\cdot$, OH' and OD' in pure water were calculated and a connection with reaction velocity was discussed.

I wish to thank Professor Svedberg, on whose suggestion this investigation was made, for his kind interest in the execution of it.

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THE DISSOCIATION CONSTANTS OF SOME POLYBASIC ACIDS.—PART III.

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In strict comparison of the several dissociation constants of an acid, either with each other or with those of another acid, the thermodynamic constants should be used. It was not found possible, however, to determine these latter constants, so that comparisons have been instituted among constants determined in solutions of the same ionic strength. This method seems likely to be fairly satisfactory, especially in the case of the corresponding constants of isomeric acids, which would be expected to have very nearly the same activity corrections. The ionic strength used for the purpose of comparison was $\mu = 0{\cdot}03$, and the assumption was made that the ionic strength at which a constant was determined was the same as that at the point in the corresponding region of the curve which was used in its calculation. The table contains the values obtained. The acids * are arranged in the order of magnitude of the "last" dissociation constants which would be expected from a consideration of the number and positions of the negative charges on the dissociating ions.

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* Benzoic acid (*Benzene monocarboxylic acid*) Phthalic acid (*Benzene* 1 : 2 *dicarboxylic acid*) Iso-phthalic acid (*Benzene* 1 : 3 *dicarboxylic acid*)
Hemi-mellitic acid (*Benzene* 1 : 2 : 3 *tricarboxylic acid*) Trimellitic acid (*Benzene* 1 : 2 : 4 *tricarboxylic acid*) Trimesic acid (*Benzene* 1 : 3 : 5 *tricarboxylic acid*)
Mellophanic acid (*Benzene* 1 : 2 : 3 : 4 *tetracarboxylic acid*) Prehnitic acid (*Benzene* 1 : 2 : 3 : 5 *tetracarboxylic acid*) Pyromellitic acid (*Benzene* 1 : 2 : 4 : 5 *tetracarboxylic acid*)
Benzene pentacarboxylic acid. Mellitic acid (*Benzene hexacarboxylic acid*

Before the values given in the table are discussed, two relationships connecting "gross constants" with "partial constants" may first be given.

DISSOCIATION CONSTANTS OF BENZENE CARBOXYLIC ACIDS AT AN IONIC STRENGTH OF 0·03.

Acid	k_1	k_2	k_3	k_4	k_5	k_6
Benzoic . . .	$6·8 \times 10^{-5}$					
Iso-Phthalic . .	$3·5 \times 10^{-4}$	$3·5 \times 10^{-5}$				
Trimesic . . .	$7·5 \times 10^{-4}$	$1·28 \times 10^{-4}$	$2·0 \times 10^{-5}$			
Phthalic . . .	$1·05 \times 10^{-3}$	$5·2 \times 10^{-6}$				
Trimellitic . .	$3·0 \times 10^{-3}$	$1·45 \times 10^{-4}$	$6·3 \times 10^{-6}$			
Pyromellitic . .	$1·20 \times 10^{-2}$	$1·34 \times 10^{-3}$	$3·2 \times 10^{-5}$	$2·35 \times 10^{-6}$		
Hemi-Mellitic . .	$1·60 \times 10^{-3}$	$6·3 \times 10^{-5}$	$1·35 \times 10^{-6}$			
Prehnitic . . .	$4·2 \times 10^{-3}$	$3·1 \times 10^{-4}$	$3·6 \times 10^{-5}$	$1·55 \times 10^{-6}$		
Mellophanic . .	$8·8 \times 10^{-3}$	$5·6 \times 10^{-4}$	$1·87 \times 10^{-5}$	$6·1 \times 10^{-7}$		
Benzene pentacarboxylic	$1·60 \times 10^{-2}$	$1·65 \times 10^{-3}$	$1·08 \times 10^{-4}$	$5·6 \times 10^{-6}$	$3·5 \times 10^{-7}$	
Mellitic . . .	$4·0 \times 10^{-2}$	$6·4 \times 10^{-3}$	$4·9 \times 10^{-4}$	$1·65 \times 10^{-5}$	$1·28 \times 10^{-6}$	$1·10 \times 10^{-7}$

(1) If we consider an acid, HA, which can split off a hydrogen ion in 'r' different ways forming the singly charged ions $A_1, A_2, A_3, \ldots A_r$, we have :—

$$ {}_1k_1 = \frac{[\dot{H}][A_1]}{[HA]}; \quad {}_2k_1 = \frac{[\dot{H}][A_2]}{[HA]}; \quad \ldots {}_rk_1 = \frac{[\dot{H}][A_r]}{[HA]} \quad . \quad (1) $$

$$ \text{and } k_1 = \frac{[\dot{H}][A_1 + A_2 + A_3 + A_4 + \ldots A_r]}{[HA]} = {}_1k_1 + {}_2k_1 + \ldots {}_rk_1. $$

The primary gross constant is thus equal to the sum of the primary partial constants.

(2) If we consider an unsymmetrical n-valent ion, A, containing only ionised carboxyl groups, and suppose that there are 'r' different ions, $HA_1, HA_2, \ldots HA_r$, from which it can be formed by the ionisation of a carboxyl group, then on applying the Law of Mass Action to the 'r' different processes, we have :—

$$ {}_1k_n = \frac{[\dot{H}][A]}{[HA_1]}; \quad {}_2k_n = \frac{[\dot{H}][A]}{[HA_2]}; \quad \ldots {}_rk_n = \frac{[\dot{H}][A]}{[HA_r]} $$

$$ \text{or} \quad \frac{1}{{}_1k_n} = \frac{[HA_1]}{[\dot{H}][A]}; \quad \frac{1}{{}_2k_n} = \frac{[HA_2]}{[\dot{H}][A]}; \quad \ldots \frac{1}{{}_rk_n} = \frac{[HA_r]}{[\dot{H}][A]}. $$

We have also

$$ k_n = \frac{[\dot{H}][A]}{[HA_1 + HA_2 + \ldots HA_r]} $$

$$ \text{or} \quad \frac{1}{k_n} = \frac{[HA_1]}{[\dot{H}][A]} + \frac{[HA_2]}{[\dot{H}][A]} + \ldots \frac{[HA_r]}{[\dot{H}][A]} $$

$$ = \frac{1}{{}_1k_n} + \frac{1}{{}_2k_n} + \ldots \frac{1}{{}_rk_n} \ . $$

It follows that the value of the gross n^{th} constant of an n-basic acid is always smaller than any of the partial n^{th} constants.

Equations (1) and (2) establish relationships between the gross and partial values of the primary and n^{th} constants of an n-basic acid. It is not possible to relate the gross and partial constants of the intermediate constants in so simple a manner, except in the case when one of the ions involved in the equilibrium can exist in only one form, as is the case with k_2 and k_3 for pyromellitic acid. In the general case, the other constants also appear in the expressions, and this complicates matters considerably. The relationships in the case of an unsymmetrical tribasic acid have been worked out by Bjerrum.[1]

Statistical Treatment of Dissociation Constants and its Application to the Benzene Carboxylic Acids.

If we could assume that, under the same conditions, a carboxyl group always ionises and re-forms at a rate which is independent of the molecule or ion to which it is attached and is uninfluenced by the presence of unionised or ionised carboxyls in the latter, then the relative theoretical values of dissociation constants may be calculated as follows.

If we consider the ionisation of an ion derived from an n-basic acid, the ion containing a unionised carboxyls and hence $(n - a)$ ionised carboxyls, then, if v_1 is the rate of dissociation of a carboxyl group, and v_2 the rate of formation of a carboxyl group from an ionised carboxyl group and $\dot{H}$ when there is one of each in a litre of solution, then the Law of Mass Action takes the form :—

$$a \, . \, v_1 \, . \, N_0 \, . \, [A^{(n-a)-}] = (n - a + 1) \, . \, v_2 \, . \, N_0^2 \, . \, [A^{(n-a+1)-}][\dot{H}]$$

and hence

$$k_{n-a+1} = \frac{[A^{(n-a+1)-}][\dot{H}]}{[A^{(n-a)-}]} = \frac{a}{(n - a + 1)} \times \frac{v_1}{N_0 v_2}$$

where N_0 is Avogadro's number.

But v_1/N_0v_2 is the dissociation constant of a single carboxyl group if the concentrations are in mols/litre, and if this is denoted by $k_{(\text{carboxyl})}$, then

$$k_{n-a+1} = \frac{a}{(n - a + 1)} \times k_{(\text{carboxyl})} \quad . \quad . \quad . \quad (3)$$

The assumption made above, that the dissociation constant of a carboxyl group is independent of the molecule to which it is attached, is obviously far-fetched. For our present purposes it will be sufficient to assume that the dissociation constant of a carboxyl group is independent of the presence of other ionised or unionised carboxyl groups in the same molecular skeleton. On this assumption, the relationship $k_1/k_2 = 4$ for dibasic acids is readily found from (3). This becomes :—

$$k_1 = k_{2-2+1} = \frac{2}{2 - 2 + 1} \times k_{(\text{carboxyl})} = 2k_{(\text{carboxyl})}$$

and

$$k_2 = k_{2-1+1} = \frac{1}{2 - 1 + 1} = \frac{1}{2} \, . \, k_{(\text{carboxyl})}.$$

Thus

$$k_1/k_2 = 4.$$

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[1] *Z. physikal. Chem.*, 1923, 106, 219.

In the case of the benzene carboxylic acids, if we assume that $k_{(\text{carboxyl})} = k_{(\text{benzoic acid})}$, then

$$k_{n-a+1} = \frac{a}{(n - a + 1)} \times k_{(\text{benzoic})}.$$

This equation shows that purely statistical considerations lead to the following relations among the dissociation constants:

$$k_{1(\text{mellitic})} : k_{1(\text{benz. pentacarboxylic})} : k_{1(\text{mellophanic})} : k_{1(\text{prehnitic})} : k_{1(\text{pyromellitic})} : k_{1(\text{h-mellitic})} : k_{1(\text{trimellitic})} : k_{1(\text{trimesic})} : k_{1(\text{phthalic})} : k_{1(\text{iso-phthalic})} : k_{1(\text{benzoic})} = 6 : 5 : 4 : 4 : 4 : 3 : 3 : 3 : 2 : 2 : 1,$$

and

$$k_{1(\text{benzoic})} : k_{2(\text{iso-phthalic})} : k_{2(\text{phthalic})} : k_{3(\text{trimesic})} : k_{3(\text{trimellitic})} : k_{3(\text{h-mellitic})} : k_{4(\text{pyromellitic}} : k_{4(\text{prehnitic})} : k_{4(\text{mellophanic})} : k_{5(\text{benz. pentacarboxylic})} : k_{6(\text{mellitic})} = 6 : 3 : 3 : 2 : 2 : 2 : 1\tfrac{1}{2} : 1\tfrac{1}{2} : 1\tfrac{1}{2} : 1\tfrac{1}{5} : 1.$$

The ratios observed, however, are very different and are of the order of

$$590 : 240 : 130 : 62 : 180 : 24 : 45 : 11 : 15 : 5 : 1$$

and $$620 : 320 : 47 : 180 : 57 : 12 : 21 : 14 : 5{\cdot}5 : 3 : 1$$

respectively.

The differences between the calculated and observed values may be ascribed in the first case to the mutual promoting effect of unionised carboxyl groups, and in the second case to the inhibiting effect of ionised carboxyl groups. In the case of *iso*-phthalic and trimesic acids the carboxyls are in the *meta*-position to each other, and hence the conditions assumed above would be expected to apply more nearly than in other acids having at least one group with a neighbour in the *ortho*-position; good agreement is, in fact, obtained in the case of k_n, and hence the conclusion can be drawn that an ionised carboxyl group in the *meta*-position has little inhibiting effect on the ionisation of another carboxyl group.

We can extend these statistical considerations further, if we assume definite rates of ionisation for carboxyl groups when others, whether ionised or unionised, are present in certain positions in the molecule. Thus, if v_1^0 is the rate of ionisation of a carboxyl group in the presence of a single ionised carboxyl group, as in *ortho*-phthalic acid, and v_2^0 is the rate of formation of the original ion, then we have:

$$k_2 = \frac{[\text{A}''][\dot{\text{H}}]}{[\text{AH}']} = \frac{1}{2} \cdot \frac{v_1^0}{v_2^0}.$$

In the case of the last stage of ionisation of pyromellitic acid, a process which can occur in only one way, the ionising carboxyl has one ionised carboxyl group in the *ortho*-position, a second in the *meta*-position, and a third in the *para*-position. The effect of an ionised carboxyl group in the *meta*-position is small, and in the *para*-position it may be expected to be even smaller; we can thus assume with some probability that the rate of ionisation will be approximately v_1^0, and the rate of formation of the original ion (with the hydrogen on the same carboxyl group) will be approximately v_2^0. Then we have

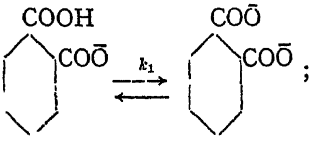
$$k_4 = \frac{[\text{A}''''][\dot{\text{H}}]}{[\text{AH}''']} = \frac{1}{4} \cdot \frac{v_1^0}{v_2^0}$$

and hence

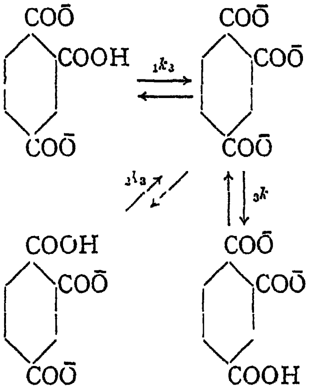
$$\frac{k_{2(\text{phthalic})}}{k_{4(\text{pyromellitic})}} = \frac{2}{1}.$$

The ratio of the experimental values is $\dfrac{5{\cdot}2 \times 10^{-6}}{2{\cdot}35 \times 10^{-6}} = \dfrac{2{\cdot}2}{1}$.

The application of such considerations to all the constants is limited by the multiplicity of processes that most of the constants represent, but in some cases quite reasonable approximations can be made. For example, we may compare the last stages of dissociation of *ortho*-phthalic and trimellitic acids:



;



It has already been stated that the effect of an ionised carboxyl in the *meta*- or *para*-position is very small, so that we should expect the relation:

$$_1k_3 \simeq {}_2k_3 \simeq {}_2k_2.$$

We have also:

$$\frac{1}{k_3} = \frac{1}{_1k_3} + \frac{1}{_2k_3} + \frac{1}{_3k_3}.$$

Again, $_3k_3$ is likely to be large in comparison with $_1k_3$ and $_2k_3$, as there is no ionised carboxyl in the *ortho*-position, so that

$$\frac{1}{k_3} \simeq \frac{1}{_1k_3} + \frac{1}{_2k_3} \simeq \frac{2}{_1k_3}$$

or

$$k_3 \simeq \frac{_1k_3}{2} \simeq \frac{_2k_2}{2} = k_2.$$

The experimental values are: $k_3 = 6{\cdot}3 \times 10^{-6}$, $k_2 = 5{\cdot}2 \times 10^{-6}$. Actually k_2 should be a little larger than k_3, but the small discrepancy is probably caused by the fact that no activity corrections have been applied. Similar considerations show that in the case of prehnitic and hemimellitic acids, $k_4^{p} \simeq k_3^{h}$, which is in agreement with the experimental results. Other deductions in agreement with experiment are: *

$k_4^{m.p.} \simeq k_3^{h}$, $k_3^{h} \simeq 3k_5^{b.p.}$, and to a lower degree of approximation: $k_5^{b.p.} \simeq 2k_6^{m}$, and $k_3^{h} \simeq 6k_6^{m}$.

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* *m.p.* = mellophanic, *m.* = mellitic, *b.p.* = benzene pentacarboxylic, acids.

In the deduction of the above results it has been assumed, where it is necessary, that the influence of a single ionised carboxyl in the *meta-* or *para-*position is negligible. In the case of mellitic acid, however, there are two ionised carboxyl groups in the *meta-*positions and another in the *para-*position, and similar complications appear in the case of benzene pentacarboxylic acid. The influence of these groups has been neglected and, as might be expected, the approximations are not so good in these cases. The influence of groups in the *meta-*position cannot be evaluated, as the data available are not sufficiently accurate, but it is certainly small. The small effect of an ionised carboxyl in the *para-*position also at present eludes quantitative determination.

The above results lead to the conclusions that the inhibiting effect of ionised carboxyl groups on dissociation is simply a function of their number and distance from the dissociating carboxyl group, and that from the magnitude of the " last " dissociation constant of certain members of a series it is possible to predict the approximate magnitude of the " last " dissociation constants of other members of the series. When the mutual " promoting " effect of carboxyl groups is considered, however, the results are not so simple, and the magnitudes of k_1 for the acids of the series show deviations from the expected order. Thus, k_1 for trimellitic acid is about twice as great as k_1 for hemi-mellitic acid, in which the groups are closer together, and similarly k_1 for pyromellitic acid is greater than k_1 for mellophanic acid, where again there is greater propinquity of the groups. Ostwald's factor law[2] cannot be applied even approximately to the type of mutual promoting effect of carboxyl groups exemplified by the acids under consideration.

If an ionised carboxyl group is regarded as an ordinary substituent, and Ostwald's factor law is applied to the comparison of $k_{1(\text{benzoic})}$ with $k_{3(\text{hemi-mellitic})}$ it is found that, when 0·153 is taken as the factor for *ortho-*substitution (a value obtained by comparing $k_{1(\text{benzoic})}$ with $k_{2(\text{phthalic})}$), the value of k_3 should be given (neglecting *meta-*influence) by:

$$\frac{1}{k_3} = \frac{1}{6{\cdot}8 \times (\cdot 153)^2 \times 10^{-5}} + \frac{2}{6{\cdot}8 \times (\cdot 153) \times 10^{-5}} = 1{\cdot}22 \times 10^{-6}.$$

The experimental value is $1{\cdot}35 \times 10^{-6}$, and it thus seems that the factor law can be applied to ionised carboxyl groups. This result seems sufficiently interesting to merit further discussion.

Thermodynamic Disscussion.

Let it be assumed that the only difference in the work which must be done in removing a proton from benzoic acid and from a singly charged phthalate ion is the electrical work due to the charge on the latter. Suppose the potential due to this charge at the point occupied by the dissociating proton is ϕ. The thermodynamic relation between the maximum work, A_T, and the equilibrium constant is (with unit arbitrary terminal concentrations) :

$$RT \ln K = A_T.$$

Hence

$$RT\,[\ln K_{(\text{benzoic})} - \ln 2K_{2(\text{phthalic})} = A_{T(\text{benzoic})} - A_{T(\text{phthalic})} = N_0 \,.\, \epsilon \,.\, \phi.$$

---

[2] *Z. physikal. Chem.*, 1889, 3, 415.

Hence

$$\ln \frac{K_{(\text{benzoic})}}{2K_{2(\text{phthalic})}} = \frac{N_0 \,.\, \epsilon \,.\, \phi}{RT}$$

or

$$K_{(\text{benzoic})} = 2K_{2(\text{phthalic})} \,.\, e^{\frac{N_0 \,.\, \epsilon \;\phi}{RT}}$$

where ϵ = elementary electric charge, and N_0 = Avogadro's number. The factor $2K_{2(\text{phthalic})}$ occurs in the above equations instead of K_2 because the measured value of K_2 is only half the value for a single carboxyl in which the proton can return to only one position, as is required by the thermodynamic discussion.

It will be observed that the factor $e^{\frac{N_0 \,.\, \epsilon \,.\, \phi}{RT}}$ corrects the statistical relationship

$$K_{(\text{benzoic})} = 2K_{2(\text{phthalic})}$$

for the effect of the electric charge on the univalent phthalate ion. The factor for *ortho*-substitution of a COŌ group, which we took as $\frac{2K_{2(\text{phthalic})}}{K_{(\text{benzoic})}}$ is clearly $e^{-\frac{N_0 \,.\, \epsilon \,.\, \phi}{RT}}$.

If we assume the statistical relationship

$$K_{1(\text{phthalic})} = 2K_{(\text{benzoic})}$$

it follows that for phthalic acid

$$K_1/K_2 = 4e^{\frac{N_0 \,.\, \epsilon \,.\, \phi}{RT}}$$

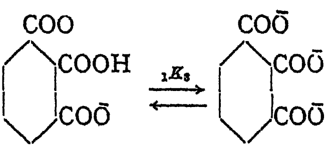
which is Bjerrum's (or Ingold's) equation. Our assumption

$$K_{1(\text{phthalic})} = 2K_{(\text{benzoic})},$$

is identical with that tacitly made by Bjerrum, *viz.* that the only difference in the work of removing a proton from phthalic acid and from the univalent phthalate ion is the electrical work done against the charge on the latter. It is interesting to note that the above deduction does not require the explicit use of Boltzmann's equation.

A similar comparison of the value of $K_{(\text{benzoic})}$ with ${}_1K_{3(\text{hemi-mellitic})}$ leads to the equation:

$$K_{(\text{benzoic})} = {}_1K_{3(\text{h-mellitic})} \,.\, e^{\frac{N_0 \,.\, \epsilon \,.\, \phi'}{RT}}$$



where ϕ' is the potential at the dissociating carboxyl group due to two negative charges in the two *ortho*-positions. This potential, however, is clearly twice that due to a charge in only one *ortho*-position, *i.e.*,

$$\phi' = 2\phi$$

and so

$$K_{(\text{benzoic})} = {}_1K_{3(\text{h-mellitic})} \,.\, e^{\frac{2N_0 \,.\, \epsilon \,.\, \phi}{RT}}$$

or

$$\frac{{}_1K_{3(\text{h-mellitic})}}{K_{(\text{benzoic})}} = e^{-\frac{2N_0}{RT}}$$

Thus the factor for double *ortho*-substitution is

$$e^{-\frac{2N_0\,\epsilon.\phi}{RT}} = e^{-\frac{N_0.\epsilon\,\phi}{RT}} \times e^{-\frac{N_0\,\epsilon.\phi}{RT}}$$
$$= (\text{factor for } \textit{ortho}\text{-substitution})^2$$

which is what we assumed in the application of the factor law to calculate $k_{3(\text{h-mellitic})}$.

Bjerrum[1] and Gane and Ingold[3] assumed, as already pointed out, that the only difference in the work of removing a proton from a dibasic acid and from its singly charged anion is the electrical work due to the charge on the latter, whereas we have taken this electrical work as equal to the difference in the work of removing a proton from the corresponding monobasic acid and the singly charged anion of the dibasic acid. In cases where the carboxyl groups are a considerable distance apart there is little to choose between the two assumptions, but when the carboxyl groups are close together, as in phthalic acid, and the first carboxyl group to dissociate is greatly aided by the presence of the second, our assumption seems preferable. The fact that two carboxyl groups in close proximity mutually influence each other in promoting ionisation is shown by the great increase in the value of k_1 for phthalic acid ($1{\cdot}05 \times 10^{-3}$) as compared with that of benzoic acid ($6{\cdot}8 \times 10^{-5}$); when one of these carboxyl groups has ionised it seems almost certain that the second one will dissociate under very different conditions, quite apart from the existence of the negative charge. One carboxyl may promote the ionisation of another :—

(1) By effects transmitted through the atom chain (electromeric effects).

(2) By external interaction between the carboxyl groups, *e.g.* dipole interaction.

(3) By means of solvation effects.

The electromeric effects are responsible for the increase in the value of k_1 for phthalic acid seems unlikely, since maleic and fumaric acids have atom chains of the same length and practically the same as in phthalic acid, although the valency link in the benzene ring of the latter is somewhat different, yet the two acids have very different values of k_1, *viz.* $1{\cdot}42 \times 10^{-2}$ and $9{\cdot}50 \times 10^{-4}$, respectively. A rough calculation using the most favourable assumptions (*i.e.* dipole orientation to produce maximum effect), showed that external dipole interaction could not explain the increase, and so it seems that it must be largely due to solvation effects. The free energy changes accompanying solvation are taken into consideration in the thermodynamic[4] relationship $A_T = RT \ln K$, although the exact mechanism by which solvation influences dissociation is not clear. It is interesting to note that acids with carboxyl groups in the *ortho*-position are more soluble than others; thus *ortho*-phthalic acid is more soluble than benzoic acid and *meta*- and *para*-phthalic acids; hemi-mellitic acid is more soluble than trimesic acid, etc. Since solubility is probably intimately connected with solvation, it would seem that acids with carboxyl groups in the *ortho*-position are more highly solvated than others.

If 'r' is calculated for phthalic acid using Ingold's value for ϕ on the two different assumptions which have been described, the following values are obtained :—

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[3] *J. Chem. Soc.*, 1931, 2153.

[4] See, for example, Smallwood, *J. Amer. Chem. Soc.*, 1932, **54**, 3048.

Bjerrum and Ingold	3·76 × 10^{-8} cm.
Present paper	5·07 × 10^{-8} cm.
Molecular Model	3·90 × 10^{-8} cm.

These results are calculated by taking the carbon-carbon link in benzene as 1·36 A, the ordinary carbon-carbon link as 1·54 A, and the distance between carbon and the effective centre of the carboxyl group as 1·00 A.

The agreement with the requirements of the molecular model is decidedly better in the case of the 'r' value calculated on the usual hypothesis of Bjerrum, and in this case the magnitudes of k_n cannot be explained quantitatively by electric induction effects alone, although the latter place them in the correct order.

The authors wish to thank the Chemical Society for a grant which has helped to defray the cost of the research.

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THE MECHANISM OF SOME CATALYTIC EXCHANGE REACTIONS OF HEAVY HYDROGEN.

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The catalytic interchange of hydrogen atoms between molecular hydrogen and water has been investigated from different points of view.[1–10]

Polanyi and Horiuti [2] suggested originally that, with regard to the mechanism of this exchange reaction (*e.g.*, on Pt), the rate determining step was the ionisation of hydrogen which followed the dissociation of the hydrogen molecules. From measurements of the catalytic exchange reaction between liquid water and *ortho*-deuterium, A. Farkas [3] showed that the ionisation mechanism is not tenable in its original form, but rather that the dissociation of molecular hydrogen is the rate determining step and that this is rapidly followed by the ionisation. The same result was obtained independently by Polanyi and Eley,[4] and Horiuti and Okamoto [5–7] were led to similar conclusions.

The purpose of the present paper is to supply further material for the elucidation of the mechanism of this catalytic reaction, by comparing the exchange reaction in the vapour and liquid phase, by varying the

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[1] J. Horiuti and M. Polanyi, *Nature*, 1935, **132**, 819 and 931.

[2] J. Horiuti and M. Polanyi, *Mem. Proc. Manchester Lit. Phil. Soc.*, 1934, **78**, 47.

[3] A. Farkas, *Trans. Faraday Soc.*, 1936, **32**, 922.

[4] D. Eley and M. Polanyi, *ibid.*, 1388.

[5] (*a*) J. Horiuti and G. Okamoto, *Sc. Pap. I.P.C.R.*, 1936, 28, 231. (*b*) G. Okamoto, J. Horiuti and K. Hirota, *ibid.*, **29**, 223.

[6] K. Hirota and J. Horiuti, *ibid.*, **30**, 151.

[7] J. Horiuti and G. Okamoto, *Trans. Faraday Soc.*, 1936, **32**, 1492.

[8] A. Farkas and L. Farkas, *ibid.*, 1934, **30**, 1671.

[9] K. F. Bonhoeffer and K. Rummel, *Naturwiss.*, 1934, **22**, 45.

[10] M. Calvin, *Trans. Faraday Soc.*, 1936, **32**, 1428.

exchange partner, and by comparing systematically the exchange reaction and the *ortho-para*-hydrogen conversion.

1. Experimental Arrangement.

The reaction vessel used is shown in Fig. 1. It had a volume of about 15 c.c. The platinum foil (10 × 10 mm., 0·1 mm. thick) Pt, used as catalyst after having been platinised (2-3 minutes, 30 mA), was mostly kept at room temperature, but one of the reaction vessels was fitted with a heating jacket. The exchange partner (2-3 c.c. water, alcohol, acetone, or the like) was placed in one limb of the vessel and by turning the vessel around the horizontal axis it was possible to investigate the exchange reaction with the vapour or with the liquid. The reaction vessel could be detached from the apparatus and shaken.

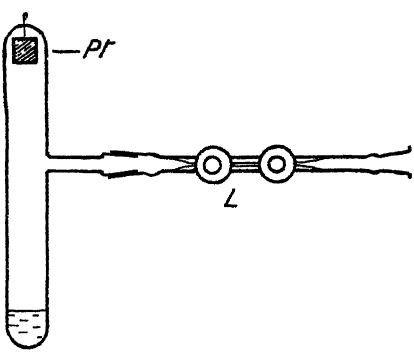

FIG. 1.

The exchange reaction was investigated in the usual way: by introducing a certain pressure of heavy hydrogen of known D-content and following up the decrease of its D content by extracting small samples by means of the capillary lock L. In a few experiments heavy water and ordinary hydrogen were used as exchange partners. The vapour pressure of the reaction partner was regulated by keeping it at different temperatures.

The platinised platinum foil could be easily prepared, it did not contain or take up an appreciable amount of hydrogen, and its activity was reasonably steady even if one exchange partner was removed from the vessel, the vessel washed and dried and another introduced. The activity of the freshly prepared catalyst was usually rather high but it soon settled to a lower value, which was then quite steady for a week or so. Poisoning of the catalyst by Hg or tap grease was prevented by not letting the catalyst stand *in vacuo* but leaving always some gas in the vessel.

The *para*-hydrogen and heavy hydrogen were prepared in the usual way and the analysis was carried out according to the micro-conductivity [11] method after the exchange partner (water, alcohol, etc.) had been frozen out in a trap cooled by liquid air.

The water used was twice distilled. The ethyl alcohol was dried by BaO and distilled *in vacuo*. The other materials, ether, acetone, etc., were purified by the usual methods.

2. Progress of the Reaction with Time.

The progress of the exchange reaction proved to proceed in every case according to the law

$$(D)_t = (D)_0 \, e^{-kt}$$

for a reaction involving a hydrogen compound as exchange partner or according to

$$(D)_\infty - (D)_t = [(D)_\infty - (D)_0]e^{-kt}$$

for a reaction involving a deuterium compound as exchange partner. $(D)_0$, $(D)_t$ and $(D)_\infty$ denote the D countent of the hydrogen gas at the time

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[11] A. Farkas and L. Farkas, *Proc. Roy. Soc. A*, 1934, 144, 467.

$t = 0$, t and $t = \infty$ (*i.e.*, in equilibrium), respectively, and k is the velocity constant. If τ is the half-lifetime for the exchange, $k = \frac{\ln 2}{\tau} = \frac{0{\cdot}69}{\tau}$. This exponential law holds since one of the reaction partners is present in considerable excess and thus the reaction is of the first order, so far as its progress is concerned, regardless of the actual mechanism. In every experiment the progress of the exchange was followed up carefully, the exact validity of the exponential law being a sure sign of the constancy in the activity of the catalyst during the reaction. Fig. 2 shows the progress of the gaseous reaction for a mixture of 12 mm. C_2H_5OH + 24 mm. heavy hydrogen (containing 40 per cent. D) at 16° C. (curve (*a*)) and also $\log \frac{(D)_t}{(D)_0}$. (curve (*b*)) as a function of time. In each case the half-lifetime of the exchange reaction was determined graphically from the progress of the reaction.

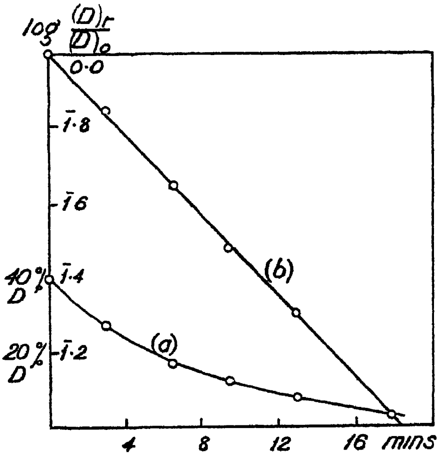

FIG. 2.

The reality of the exchange was checked by removing the exchange partner by freezing it out which caused the immediate stop of the exchange. This proves that there was no appreciable amount of hydrogen adsorbed or absorbed by the catalyst.

3. Reaction Rate in the Vapour and Liquid.

The rates of exchange in vapour and liquid water are shown in Figs. 3 and 4. Fig. 3 refers to an experiment with a very active catalyst, curve

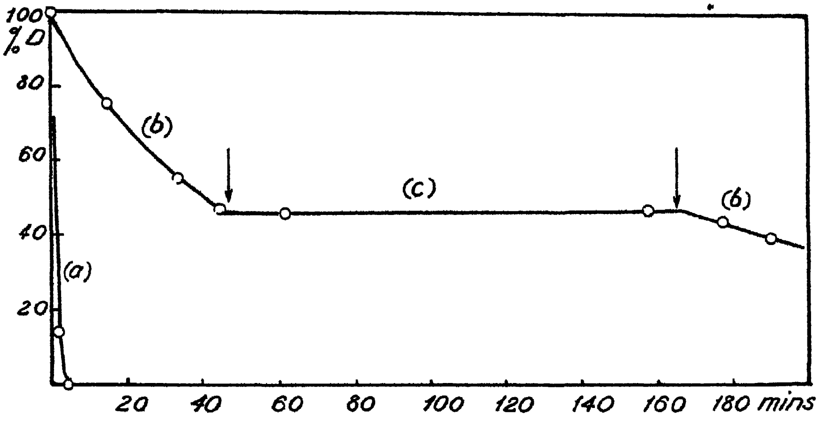

FIG. 3.

(*a*) being the rate in the vapour on a dry catalyst, curve (*b*) for the exchange with a wet catalyst, and curve (*c*) for the exchange with a catalyst under water. The conditions for curve (*b*) were obtained by removing the Pt-foil from the water by turning the vessel around the horizontal axis, the conditions for curve (*a*) by drying the catalyst. It is evident that whereas the half-lifetime of the exchange in the vapour on the dry catalyst is less than ½ minute and on the wet catlyst 40 minutes, there is practically no exchange even in two hours when the catalyst is under water. Fig. 4 shows the comparison of the exchange rates in the vapour on a dry catalyst (curve (*a*)), less active than in Fig. 3, and in the liquid with and without shaking (curves (*b*) and (*c*) respectively). From this experiment it follows that on this particular catalyst the half-lifetime for the vapour phase reaction was 12 minutes, and for the liquid phase reaction 170 minutes.

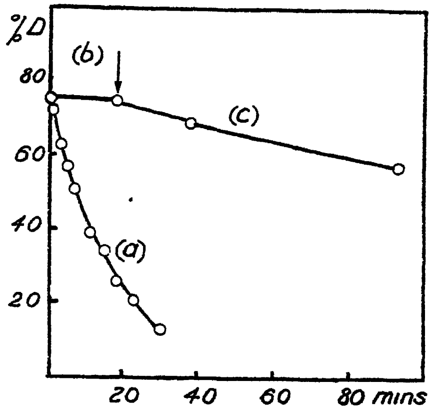

FIG. 4.

The comparison of the reaction rates in the vapour and liquid for different reaction partners is given in Table I. The catalyst was not the same for all of these reactions. The temperature of the catalyst was 18 ° C., the pressure of the hydrogen ·25 mm., and the pressure of the reaction partner in the vapour phase reaction 15-40 mm. (The acetone was cooled to reduce its vapour pressure.) The reaction vessel was strongly shaken for the investigation of the exchange in the liquid. It will be recognised that in the case of water and alcohol the reaction proceeds in the vapour phase much faster than in the liquid, whereas in the case of the acetone and benzene the difference is not so great.

TABLE I.—HALF-LIFETIMES FOR THE EXCHANGE.

No. of Experiment.	Exchange Partner.	Vapour.	Liquid.
14, 15	H_2O	12 mins.	170 mins.
74, 83	C_2H_5OH	6 ,,	40 ,,
36, 38	CH_3COCH_3	7 ,,	18 ,,
52, 53	C_6H_6	16 ,,	33 ,,

4. Comparison of Exchange Rates with Different Partners on the Same Catalyst.

In a few experiments the same vessel with the catalyst in the same state of activity was filled with different substances one after the other, and the velocity of the exchange in each case was determined. Between two fillings, the vessel was washed out and dried. In the case of the higher alcohols the washing was done with ether. The figures for half-life are given in Table II.

It is striking that the exchange with water and the alcohols proceeds approximately with similar speed, but

TABLE II.

No. of Experiment.	Exchange Partner.	Half-Lifetime (τ) of Exchange in Minutes.
115	12 mm. Water	13·5
116	16 ,, Ethylether	> 200
118	46 ,, Acetone	36
145	3 ,, *n*-Butanol	10
147	1 ,, (2)-Ethylhexanol	10·5
151	12 ,, Water	20
153	60 ,, Benzene	100

with benzene and ether, much more slowly. It should be mentioned, however, that washing and drying of the catalyst and also the inlet of air between two consecutive experiments might slightly affect the catalyst from case to case so that these figures are not to be regarded as final.

5. Comparison of the *Para*-hydrogen Conversion and Exchange Reaction.

The *para*-hydrogen conversion was compared with the exchange by measuring, immediately after the exchange experiment, the rate of *para*-hydrogen conversion in a separate run at the same temperature and pressure. The results are given in Table III.

TABLE III.

Temperature of the Catalyst 17° C.
Pressure of Hydrogen 20-30 mm. Hg.

No. of Experiment.	Pressure of Exchange Partner in mm.	Half-Lifetime (τ) in mins.		Ratio $\frac{\tau_{exch.}}{\tau_{conv.}}$
		Exchange.	Para-Conversion.	
	In the Vapour :			
116, 117	17 Ether	> 200	1	> 200
50, 51	40 Benzene	13	$< 0·5$	> 26
118, 119	8 Acetone	60	5	12
85, 86	16 Ethyl alcohol	8	4·5	1·8
114, 115	12 Water	13·5	7·4	1·8
145, 146	3 *n*-Butanol	10	6	1·6
147, 148	1 (2)-Ethyl hexanol	10	4	2·5
	In the Liquid :			
26, 27	Water	50	50	1·0
52, 53	Benzene	33	22	1·5
56, 57	Acetone	15	9·5	1·6

It will be seen that in the vapour phase in the case of water and the alcohols, and in the liquid phase in all cases, the rates of the *para*-hydrogen conversion and of the exchange do not differ much ; whereas the exchange reaction in the vapour phase with benzene, acetone and ether is very much slower than the *para*-hydrogen conversion. This is in agreement with the results of Farkas [3] and Polanyi and Eley,[4] except for the case of benzene. In this case, the latter authors found that in the liquid the *para*-hydrogen conversion proceeds about twenty times more quickly than the exchange.

It is evident that in regarding the relative rates of *para*-hydrogen conversion and of exchange we can distinguish two groups of exchange partners. The discussion (§ 8) will show, however, that this distinction is not quite strict since the relative velocities depend largely on the pressures. Therefore it is not possible to draw any conclusions with regard to the mechanism of the exchange reaction from a mere comparison of these rates. The exchange reaction involves two reactants and the relative concentration of these reactants on the catalysts are of decisive influence for the rate of exchange.

The exchange reaction of C_6H_6 and acetone appears to be complicated by hydrogenation as it was found in the case of C_2H_4.[12] Polanyi and Horiuti [13] put the theory forward that these two reactions are necessarily

[12] A. Farkas, L. Farkas, and E. K. Rideal, *Proc. Roy. Soc. A*, 1934, 146, 630.

[13] J. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, 1934, 30, 1164.

connected, since in the case of unsaturated compounds (acetone in the enol-form CH_3-CH(OH) = CH_2), both exchange and hydrogenation involve as the first step the "half hydrogenated" compound. For the moment we have no direct proof for this theory, since the relation of the rates of these two reactions could not be established. In preliminary experiments on certain catalysts the hydrogenation was negligibly small compared with the rate of exchange; in others the hydrogenation was much more rapid. Owing to this complication a more detailed investigation of the interaction of hydrogen with reducible substances will be dealt with in a forthcoming paper.

With saturated hydrocarbons such as hexane and cyclohexane an exchange was also observed with a speed of the same order of magnitude as with, *e.g.*, C_6H_6. However, it remains to be investigated whether the observed exchange was not due to some impurity present in these hydrocarbons.

6. Experiments with Alcohol.

Tables IV. and V. summarise the results obtained concerning the dependence of the rate of exchange and of conversion on the alcohol pressure. With increasing pressure the *para*-conversion shows more and more marked inhibition whereas the rate of exchange increases to a maximum and then decreases.

TABLE IV.—DEPENDENCE OF THE EXCHANGE AND OF THE PARA-CONVERSION ON THE ALCOHOL PRESSURE.

Temperature of the catalyst 19° C.
Pressure of heavy hydrogen (40 per cent. D) 20-25 mm. Hg.

No. of Experiment.	Pressure of Alcohol in mm.	Half-Lifetime (τ) in Mins.	
		Of the Exchange.	Of the *Para*-Conversion.
75	0·002	700	—
79	0·04	50	—
78	0·3	15·5	—
77	1·6	6·0	—
76	3·5	5·3	—
73	12	5·5	—
74	28	6·0	—
97, 98	0·01	200	3·5
95, 96	0·5	11·5	3·3
91, 92	3·5	9·5	5·0
93, 94	24	12·5	9·4

TABLE V.—DEPENDENCE OF THE EXCHANGE ON THE HYDROGEN PRESSURE.

Pressure of alcohol 4 mm. Hg.

No.	Pressure of Heavy Hydrogen (40 Per Cent. D) (= P) in mm. Hg.	Half-Life (τ) in Minutes.	$\frac{P}{(\tau)}$.
82	2	4·1	0·49
81	7	5·5	1·27
80	20	6·5	3·08

In order to decide which of the hydrogen atoms in the alcohol molecule take part in the exchange, an alcohol containing 33 per cent. D in the hydroxyl group (67 per cent. C_2H_5OH + 33 per cent. C_2H_5OD) was prepared by mixing alcohol with heavy water, distilling the alcohol, drying it with BaO and redistilling it *in vacuo*. This alcohol was then brought, in a reaction vessel, into contact with H_2.

The change of the D content of the hydrogen added originally is given in Table VI. This shows definitely that this catalyst does not perform the exchange of other hydrogen atoms in the alcohol than the one in the hydroxyl group, since a hydrogen containing 11·1 per cent. D is in equilibrium (assuming an equilibrium constant 1·2 [11] for the exchange between water and alcohol) with the present alcohol if only the H-atoms in the hydroxyl group are exchangeable. On the other hand, if all H-atoms would take part in the exchange the gas should not contain more than 1·5 per cent. D.

The determination of the equilibrium D content of gaseous hydrogen in contact with alcohol-water mixtures might be used for the determination of the D content of the liquid phase without having to separate the alcohol from the water. Similarly it might be used for the determination of any exchangeable H-atom in organic compounds.[15]

TABLE VI—25 mm. (33 PER CENT. C_2H_5OD + 67 PER CENT. C_2H_5OH) + 35 mm. H_2 at 17° C.

Time in Minutes.	Per Cent. D in the Hydrogen.
0	0·0
2	6·7
5	9·2
11·5	10·9
16	11·2
1200	11·1

7. Experiments with Water.

The dependence of the conversion and the exchange rate on the water vapour pressure is the same as that on the alcohol pressure. It is worth while to note the inhibition of the exchange rate by higher pressures of water vapour. The results are summarised in Table VII.

8. Discussion.

In this paragraph only the experiments with water and the alcohols will be discussed in detail, since the others are of a more preliminary character.

The most important feature which emerges is that both the hydrogen and the other reactant have to be present in the adsorption layer. This is evident from Tables IV., V. and VII., which show that (1) the rate of *para*-conversion is reduced by increasing concentration of alcohol or water, (2) the exchange rate is inhibited by a higher pressure of water or alcohol, and (3) the exchange reaction is much slower in the liquid than in the gas. All these phenomena are readily explicable if we assume that the catalytic reaction takes place in the adsorption layer and that hydrogen and alcohol or water can replace each other. According to this view the reaction does not involve interaction between adsorbed alcohol molecules and gaseous hydrogen, for example, or adsorbed hydrogen and water (or alcohol) from the liquid if we extend this assumption also to the case of the catalysis in the liquid phase.

TABLE VII.—DEPENDENCE OF THE EXCHANGE AND OF THE CONVERSION ON THE H_2O PRESSURE.

Pressure of Heavy Hydrogen 20-25 mm. Hg.

No.	Pressure of H_2O.	τ for Exchange in Mins.	τ for Conversion in Mins.
106	0·02	200	—
107	0·38	16	—
108	1·1	6·5	—
109-110	4·5	3·7	2
111	11	3·7	—
112-113	7·5	10	4·9
114-115	12	13·5	7·4
19*a*	15	48	9·5
19*b*	4·5	16	5

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[14] *Cf.* K. Wirtz, *Z. physik. Chemie, B*, 1936, **34**, 136.

[15] For the determination of the D-content of water by a similar method, *cf.* A. Farkas, *Trans. Faraday Soc.*, 1936, **32**, 413.

The mechanism of this exchange reaction can be deduced from the observation that the conversion reaction proceeds with approximately the same speed as the exchange reaction. In the gaseous phase this cannot be attributed to diffusion.

We shall now assume, as is well supported experimentally, that the conversion of *para*-hydrogen on the surface of the catalyst proceeds by dissociation of the molecules and subsequent recombination of the atoms. On the other hand, in the exchange reaction one hydrogen atom from the water or from the alcohol must take part. Consequently, the simplest explanation for the observation that the whole reaction *

$$2\mathrm{D} + \mathrm{RH} \rightarrow \mathrm{RD} + \mathrm{HD}$$

(where R designates C_2H_5O- or HO-) happens with the same speed as the recombination

$$2\mathrm{H} \rightarrow \mathrm{H}_2$$

is that either (*a*) the H-atom of the alcohol or water is just as free as the atoms formed by the dissociation of the hydrogen molecules, or (*b*) there is a very rapid exchange reaction in the adsorption layer of the type

$$\mathrm{D} + \mathrm{RH} \rightarrow \mathrm{RD} + \mathrm{H}.$$

We cannot at present decide between these two mechanisms.

We shall now consider the first explanation, since the second can be regarded formally (see below) as a special case of the first. The main feature we wish to stress is that, from a systematic comparison of the *ortho-para*-conversion rate with the exchange rate, it is possible to deduce the relative concentrations of the active reaction partners in the adsorption layer.

The first-mentioned mechanism involves the following steps :—

$$\mathrm{RH} \rightarrow \mathrm{R} + \mathrm{H} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\mathrm{D}_2 \rightarrow \mathrm{D} + \mathrm{D} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\mathrm{R} + \mathrm{H} \rightarrow \mathrm{RH} \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

$$\mathrm{R} + \mathrm{D} \rightarrow \mathrm{RD} \quad . \quad . \quad . \quad . \quad . \quad (3b)$$

$$\mathrm{H} + \mathrm{H} \rightarrow \mathrm{H}_2 \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

$$\mathrm{H} + \mathrm{D} \rightarrow \mathrm{HD} \quad . \quad . \quad . \quad . \quad . \quad (4b)$$

$$\mathrm{D} + \mathrm{D} \rightarrow \mathrm{D}_2 \quad . \quad . \quad . \quad . \quad . \quad (4c)$$

All these steps are assumed to take place in the adsorption layer. If we put k_1 and k_2 as the velocity constant for the dissociation reactions 1) and (2), and k_3 and k_4 for the recombination reactions (3) and (4) respectively (neglecting the difference between the individual recombination constants for (3*a*) and (3*b*), (4*a*), (4*b*), and (4*c*), we find

$$k_1[\mathrm{RH}] = k_3[\mathrm{R}]\{[\mathrm{H}] + [\mathrm{D}]\} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$k_1[\mathrm{RH}] = k_4\{[\mathrm{H}]^2 + [\mathrm{H}]\,[\mathrm{D}]\} + k_3[\mathrm{R}]\,[\mathrm{H}] \quad . \quad . \quad . \quad (6)$$

$$k_2[\mathrm{D}] = k_4\{[\mathrm{D}]^2 + [\mathrm{H}]\,[\mathrm{D}]\} + k_3[\mathrm{R}]\,[\mathrm{D}] = k_4\{[\mathrm{H}] + [\mathrm{D}]\}^2 \quad (7)$$

$$[\mathrm{R}] = \frac{k_1[\mathrm{RH}]}{k_3\{[\mathrm{H}] + [\mathrm{D}]\}} = \frac{k_1[\mathrm{RH}]\sqrt{k_4}}{k_3\sqrt{k_2[\mathrm{D}_2]}} \quad . \quad . \quad . \quad . \quad (8)$$

$$[\mathrm{H}] = \frac{k_2[\mathrm{RH}]}{k_1[\mathrm{RH}] + k_2[\mathrm{D}_2]}\sqrt{\frac{k_2[\mathrm{D}_2]}{k_4}} \quad . \quad . \quad . \quad . \quad (9)$$

$$[\mathrm{D}] = \frac{k_2[\mathrm{D}_2]}{k_1[\mathrm{RH}] + k_2[\mathrm{D}_2]}\sqrt{\frac{k_2[\mathrm{D}_2]}{k_4}}. \quad . \quad . \quad . \quad . \quad (10)$$

---

* Hereafter we shall use H and D in general to designate the hydrogen atoms of the water (or alcohol) and that of the gaseous hydrogen respectively.

The apparent conversion (C) and exchange (E) is

$$C = k_2[D_2] = k_4\{[H] + [D]\}^2 \quad . \quad . \quad . \quad . \quad (11)$$

$$E = k_3[R][D] = k_4\{[H]^2 + [H][D]\} = \frac{k_1[RH] \, . \, k_2[D_2]}{k_1[RH] + k_2[D_2]} \quad (12)$$

Since in the actual experiment D_2 was replaced by p-H_2 to measure the *para*-conversion, [H] + [D] represents the total atomic concentration, *i.e.*, the sum of that resulting from the dissociation of H_2 and RH. As will be shown the same dependence of the *para*-conversion and exchange on the concentration of the reaction partners follows as has actually been observed.

We distinguish two cases :

$$(a) \ \frac{k_1[RH]}{k_2[D_2]} > 1 \qquad \text{and} \qquad (b) \ \frac{k_1[RH]}{k_2[D_2]} < 1$$

For given k_1 and k_2 these two cases can be realised if RH or D_2 is present in great excess in the adsorption layer. For case (*a*), RH in excess, we find from equations (11) and (12) that the exchange and *para*-conversion are equal $C = E = k_2[D_2]$, *i.e.*, proportional to the amount D_2 adsorbed. This explains the dependence of the exchange in Table V, when the surface is mainly covered by RH and the adsorbed amount of D_2 (or P/τ) is nearly proportional to the hydrogen pressure. In the same way we can explain the inhibition of the *para*-conversion and also that of the exchange itself by increasing RH pressures (Tables IV. and VII.) when D_2 is replaced by RH and [D] is decreasing. For case (*b*), the exchange reaction is proportional to the amount of RH adsorbed and the *para*-conversion to the amount of hydrogen adsorbed. This case is realised for low pressures of RH (see Table IV.).

From the speeds of the *para*-conversion (C) and the exchange (E) it is possible by combining equations (5) to (12), to deduce the relative concentrations of each partner in the adsorption layer in dependence of the pressure and to obtain thus a detailed picture of the adsorption layer. We find

$$[RH] \propto CE/(C - E) \quad . \quad . \quad . \quad (13)$$

$$[D_2] \propto C \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

$$[R] \propto \sqrt{C}E/(C - E) \quad . \quad . \quad . \quad (15)$$

$$[H] \propto E/\sqrt{C} \quad . \quad . \quad . \quad . \quad (16)$$

$$[D] \propto (C - E)/\sqrt{C} \quad . \quad . \quad . \quad (17)$$

This calculation naturally involves the error caused by putting the recombination constants for equations (4*a*), (4*b*) and (4*c*) equal, which can be estimated if the *para*-conversion and exchange are measured by comparing also the reaction p-H_2 + RD with that n-H_2 + RD and not only p-H_2 + RH with n-D_2 + RH. In this case (and also in the systems o-D_2+RH, n-D_2 + RH), however, the conversion rate does not include any recombination between H and D atoms but only those between two H-atoms.

TABLE VIII.—THE CONCENTRATION (IN ARBITRARY UNITS) OF THE REACTANTS IN THE ADSORPTION LAYER IN DEPENDENCE OF THE ALCOHOL PRESSURE.

No.	C_2H_5OH in mm. Hg.	$[D_2]$.	[RH].	[R].	[H].	[D].
97, 98	0·01	28·6	0·51	0·09	0·09	5·26
95, 96	0·5	31·5	12·0	2·15	1·55	4·06
91, 92	3·5	20·0	22·2	4·98	2·35	2·13
93, 94	24	10·6	32·7	10·0	2·46	0·79

Table VIII., in which these quantities are listed, shows that the concentrations of [RH], [R] and [H] gradually rise with increasing pressure of RH and [D_2] and [D] are replaced in the adsorption layer.

So far as the dependence of the exchange rate on the concentration of the reaction partners is concerned, essentially the same relation is to be expected from the second mechanism as from the one just treated. Calculation of the concentration of the active reaction partners in the adsorption layer from the rate of the conversion and exchange also gives similar formulæ, the only difference being that in this case

$$[\mathrm{RH}] \propto \sqrt{C}E/(C - E).$$

A discrimination between the two mechanisms could be made at low pressure when the concentration in the adsorption layer is rather low and the concentration of one active reaction partner is not altered by the presence of the other (no displacement). Under such conditions for the case when

$$E/(C - E) > 1$$

E should be independent of C if the first mechanism is operative but should be proportional to $\sqrt{C}$ if the second mechanism is valid. Such an investigation is planned.

The recent experiments on the catalytic exchange of hydrogen atoms between gaseous hydrogen and methane by Taylor and co-workers[16] seems to favour the dissociation mechanism (*a*). These investigators have found that an exchange of hydrogen atoms took place also between CH_4 and CD_4 even if no gaseous hydrogen was added. Since it is improbable that this reaction is due to some residual amount of hydrogen present in the catalyst, the $CH_4 + CD_4$ exchange can be very safely considered to take place through the dissociation mechanism.

This mechanism is also in general agreement with that proposed previously for the catalytic exchange of hydrogen atoms between water vapour and molecular hydrogen on a heated platinum filament,[8] if we allow for the difference in the relative concentrations of the reactions partners in the adsorption layer at the higher temperatures.

We are now in a position to understand why the exchange reaction proceeds so much more slowly in the liquid water or alcohol than in the vapour phase. These substances are strongly adsorbed and displace the hydrogen to a great extent on the wet catalyst. Even at higher hydrogen pressures, up to one atmosphere, the adsorption layer may be far from saturation with regard to hydrogen. One may therefore obtain any order up to unity for the dependence of the rate of exchange on the hydrogen pressure.

Whether the H atoms, or the HO, or C_2H_5O radicals formed in the dissociation of water, alcohol, etc., are neutral or ionised cannot yet be stated. Polanyi and Horiuti[1, 2] concluded originally that the catalysis occurs in the liquid by ions, since exchange was found to be different in alkaline and acid solution. According to Horiuti and Okamoto[7] this effect may be due to poisoning.

More recently, Calvin,[10] examining the effect of polarisation on the catalytic exchange reaction between water and hydrogen, found that anodic polarisation up to 3 volts had no effect on the rate of exchange but that a cathodic polarisation decreases the exchange and increases the *para*-hydrogen-conversion. From this he has concluded that the bond H—Pt must be polar. It is also possible that by the polarisation only the concentration of water is affected in the adsorption layer in a sense that it is repelled, as it were, by the negatively polarised platinum. Such an effect would of course also account for the increased *para*-conversion.

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[16] K. Morikawa, W. S. Benedict and H. S. Taylor, *J. Am. Chem. Soc.*, 1935, **57**, 592, and 1936, **58**, 1445, 1795.

It is, however, improbable that electrolytic ions as formed in solutions, play a part in catalytic exchange involving water and alcohol vapour, even if one assumes capillary condensation in the pores of catalysts. If ions are actually formed immediately after the adsorption of gaseous hydrogen on the catalyst, they must be rather of the type as postulated by O. Schmidt.[17] since, according to the argument presented above, the same particles must be formed from the hydrogen molecules as from water or alcohol in order to make the exchange reaction as fast as the conversion of *para*-hydrogen.

In comparing the catalytic exchange velocities of different partners, one has always to consider the relative concentration in the adsorption layer, and in general, it is not permissible to draw conclusions as to the mechanism from such a comparison. If we compare the relative exchange rates of the substances X and Y with water and hydrogen, we might obtain different relative velocities, even though the identical mechanism is operative in all cases of exchange, if the adsorbabilities are sufficiently different. If the adsorbabilities of these substances form a series $H_2 < X < Y < H_2O$ for example, where each substance replaces the preceding one on a catalyst at given pressure and temperature, we obtain the following exchange rates :

$$\begin{array}{ccc} (H_2 + X) & > & (H_2 + Y) \\ \vee & & \wedge \\ (H_2O + X) & < & (H_2O + Y) \end{array}$$

or in other words, X will exchange more quickly with H_2 than with H_2O, whereas for Y, just the reverse is true. In consequence, the conclusions drawn by Polanyi and co-workers [13, 18] from the cases where X and Y are C_2H_4 and C_6H_6, and C_6H_6 and cyclohexane respectively cannot be regarded as definitely proving the special mechanisms proposed for these particular reactions.*

If we extend the view proposed for the catalytic exchange between water and the alcohols and gaseous hydrogen also to the catalytic exchange involving other substances such as ether, acetone, benzene, etc., all the results obtained with these substances and listed in Tables I. to III. become understandable at least qualitatively.

In Fig. 5, Curve (1) represents the amount of dissociated molecules of the exchange partner AH and (2) the amount of dissociated molecules of hydrogen or conversion of *para*-hydrogen (see equation (11)) in dependence of the concentration of the exchange partner AH in the gas phase, *i.e.*, (1) is the curve for $k_1[AH]_{ads}$ and (2) that for $k_2[D_2]_{ads}$ if we use the symbols of formulæ (5) to (7). At small pressures of AH the amount of AH adsorbed is proportional to the pressure of AH and reaches saturation at higher pressures. At constant partial pressures of D_2 the amount of D_2 adsorbed is independent of the AH pressure at low pressures of AH, but it is gradually displaced as the concentration of AH rises in the adsorption layer. Curve (3) represents the exchange rate (E). If the adsorption of the substance AH is strong, it is already in the saturation region at the vapour pressure of AH at the temperature of the catalyst (Point P). On the other hand, with weak adsorption, the amount of AH adsorbed will be far from saturation at its vapour pressure (Point P). The transition from case where the catalyst is in contact with the vapour of AH to that when it is in contact with liquid AH is indicated by the arrows between P and K. Naturally this region between P and K is not realisable.

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[17] *E.g.*, O. Schmidt, *Z. physik. Chemie*, 1925, 118, 210; *Chemical Reviews*, 1933, 12, 363.

[18] C. Horex and M. Polanyi, *Mem. Proc. Manch. Literary and Phil. Soc.*, 1936, 80, 33.

* The possibility of a displacement was mentioned by Horiuti and Polanyi [13] who assumed, however, that in fact it does not occur.

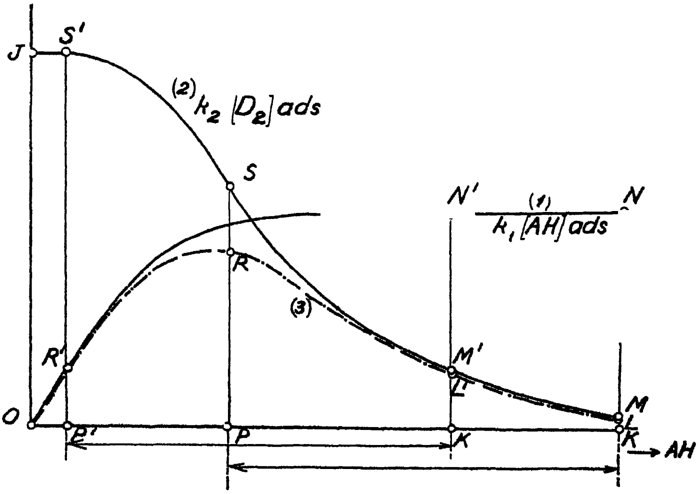

FIG. 5.

From this figure we can read off: C = rate of *para*-conversion, E = rate of exchange (the letters PS, OJ in Table IX., etc., refer to the corresponding distances in Fig. 5).

TABLE IX.

Adsorption.	$\frac{C \text{ with AH present}}{C \text{ with AH absent}}$.	E in vapour.	C/E in vapour.	$\frac{E \text{ in vapour}}{E \text{ in liquid}}$.	C/E in liquid.
Weak .	$\frac{P'S'}{OJ} \approx 1$	P'R' small	$\frac{P'S'}{P'R'} \gg 1$	$\frac{P'R'}{K'L'} \approx 1$	$\frac{K'M'}{M'L'} \approx 1$
Strong .	$\frac{PS}{OJ} < 1$	PR large	$\frac{PS}{PR} \approx 1$	$\frac{PR}{KL} \gg 1$	$\frac{KM}{KL} \approx 1$

If we regard water and the alcohols as strongly adsorbed and ether, acetone, benzene, hexane, etc., as weakly adsorbed, a comparison of these results with the data listed in Tables I. to V. and VII. will show agreement in every case. This qualitative agreement, however, does not prove the assumption that the same mechanism is operative in every case of exchange catalysis but it only supports the view as to the influence of the concentrations in the adsorption layer on the reaction velocity.

Summary.

Using a platinised platinum foil as catalyst, the exchange of hydrogen atoms between gaseous deuterium and water and some alcohols has been investigated. The rate of exchange has been compared with the rate of conversion of *para*-hydrogen at varied pressures of hydrogen and of the exchange partner. A comparison has also been made between the rate of exchange in the vapour and the liquid and between the relative exchange rates with the mentioned substances, and acetone, benzene, and ether. The results obtained are explicable by assuming the processes (R = C_2H_5O or OH, etc.).

(1) $RH \rightarrow R + H$
(2) $D_2 \rightarrow D + D$
(3) $R + D \rightarrow RD$
(4) $H + D \rightarrow HD$

in the adsorption layer. At low concentration of water or alcohol, (1) is the rate governing step, at higher concentration (2). It is shown that by comparing the rates of exchange and *para*-conversion, it is possible to deduce the relative concentrations of each of the reactants figuring in the reactions (1) to (4). The importance of the concentration of the reaction partner in the adsorption layer is stressed, and how they influence the rate of exchange and that of *para*-conversion is shown.

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THE CONTINUOUS ABSORPTION SPECTRUM OF METHYL IODIDE.

By D. Porret and C. F. Goodeve.

Received 1st *March*, 1937.

The continuous absorption spectrum of methyl iodide has been studied by Herzberg and Scheibe[1] between 35,000 and 50,000 cm.$^{-1}$; but only relative values of the extinction coefficient were obtained. Many other authors[2, 3, 4, 5, 6] have studied this spectrum in order to determine the position of the maximum or to find the long-wave absorption limit. They used the latter to calculate the heat of dissociation of the molecule. According to Iredale and Wallace[2] the limit for the liquid is at 3950 Å. and the corresponding heat of dissociation, 50 K. cals. According to Iredale and Mills[3] the limit for the gaseous state is at 3300 Å. and the heat of dissociation, 65 K. cals. Henrice found the limit at 2950 Å. It is now well known that it is practically impossible to reach a real absorption limit, and that the long-wave edge of the continuum shifts towards the red when the length of the absorption tube, or the pressure, is increased.

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[1] *Z. physik. Chem.*, 1930, **7**, 390.
[2] Iredale and Wallace, *Phil. Mag.*, 1929, **8**, 1093.
[3] Iredale and Mills, *Proc. Roy. Soc.*, *A*, 1931, **133**, 430.
[4] Henrice, *Z. Physik.*, 1932, **77**, 35.
[5] Henrice and Grieneisen, *Z. physik. Chem.*, 1935, **30**, 1.
[6] Emschwiller, *Compt. Rend.*, 1930, **191**, 208.

In this paper quantitative measurements of the absorption spectrum of methyl iodide, made over a wide range of tube lengths, are described.

Methyl Iodide.—The methyl iodide, obtained from Hopkin and Williams, was dried with P_2O_5 and fractionated three times. The boiling-point was then constant, and the substance was very stable, even under the action of U.V. light.

Apparatus.—The measurements have been made by a photographic method. Three different optical systems (light source, photometric device, cells, spectrograph, etc.) were used to cover the wide range of optical thicknesses. They are summarised in Table I.

TABLE I.

Light source	Absorption cell	Range of frequencies in cm.$^{-1}$	Method of Photometry	Spectrograph
Hydrogen discharge tube	8 cm. quartz	50,000 to 43,000	Single cell, different times	Hilger Small Quartz E 370
Iron Tungsten spark	1, 8, and 55 cm. quartz	45,000 to 30,000	Twin cells, Spekker divided beam photometer	Hilger Medium Quartz E. 3
Hydrogen discharge tube	3355 cm. glass with quartz end pieces	32,000 to 27,000	Single cell, different times	Hilger Quartz Raman E. 420

In the first and third systems, the blackening of the different spectra was compared by means of a Zeiss microphotometer. In the second system, pairs of spectra were obtained corresponding to known optical densities. The match point was determined visually.

All the results were in very good agreement even when two different methods were used for the same frequency. The measurements were carried out at room temperature (19° ± 1).

Results.

The molecular extinction coefficient, ϵ, and the absolute extinction coefficient, α, are defined by the equations,

$$\epsilon = \log_{10} \frac{I_0}{I_t} \cdot \frac{1}{c \, . \, l}$$

and

$$\alpha = \log_e \frac{I_0}{I_t} \cdot \frac{1}{n \, . \, l}$$

where I_0 and I_t are the intensities of the incident and transmitted beams, c the concentration in gr. mol. per litre, n the concentration in molecules per c.c., and l the length of the absorption column in centimeters. The ratio of the two coefficients is, $\epsilon/\alpha = 2{\cdot}63 \times 10^{20}$.

The logarithms of ϵ and α are plotted against the frequency (cm.$^{-1}$) in Fig. 1. The frequencies corresponding to the energy (approximate) required to dissociate CH_3I into $CH_3 + I\,^2P_{\frac{3}{2}}$ (58 K. cals.) and $CH_3 + I\,^2P_{\frac{1}{2}}$ (80 K. cals.) are also indicated.

Discussion.

It is seen from Fig. 1 that the extinction coefficient has a maximum value at 38,800 cm.$^{-1}$ followed by a minimum at 47,400 cm.$^{-1}$. The maximum is, according to Herzberg and Scheibe[1] at 39,400 cm.$^{-1}$, and, according to Emschwiller[6] at 38,900 cm.$^{-1}$. Other measurements of Scheibe[7] show that the maximum has the same value of ϵ and is at the same frequency, for methyl iodide in solution in hexane as in the gaseous state. He did not observe a minimum. Scheibe also points out a certain analogy between the absorption spectrum of methyl iodide and those of iodine ions and inorganic iodides in different solvents. The change of the solvent does not change either the shape of the curve or the extinction coefficient of the maximum but only its position. According to Angerer and Müller,[8] and Franck and co-workers,[9] the spectrum of gaseous iodides present also two bands with approximately the same distance between them. Scheibe, as well as Franck, explains the presence of two bands by the assumption that the light can dissociate the iodine molecules yielding normal and excited iodine atoms

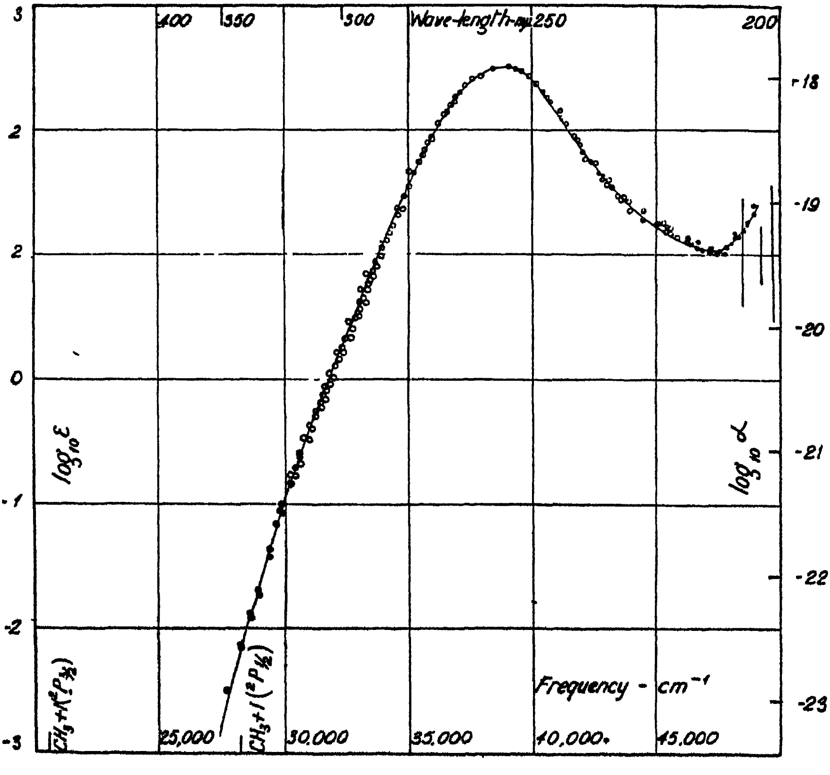

FIG. 1.—The Extinction Coefficients of CH_3I ⊖, ○ and ● indicate observations made by the first, second and third systems respectively.

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[5] *Physik. Z.*, 1925, 26, 643; *Ann. Physik.*, 1927, 82, 39.

[6] *Z. Physik*, 1927, 43, 155.

[7] *Z. Electrochem.*, 1928, 34, 497.

respectively. The energy of excitation of a $^2P_{\frac{3}{2}}$ iodine atom into a $^2P_{\frac{1}{2}}$ corresponds to 7600 cm.$^{-1}$. The distance between the two maxima for dissolved iodides is actually about 7600 cm.$^{-1}$.

The absorption spectrum of CH_3I is continuous indicating that the molecule dissociates on the absorption of a quantum of light, most likely into a CH_3 radical and an iodine atom. The low quantum efficiency for decomposition would appear to exclude the possibility of dissociation into CH_2 and HI. There has already been much speculation as to the electronic states of the products. From the absence of the second absorption band in his methyl iodide spectrum and from the lowering of the first one in certain salts (HgI_2, CdI_2), Scheibe concluded that the band of methyl iodide corresponded to the second one of inorganic iodides, *i.e.*, to a dissociation into CH_3 and excited iodine atoms. Our curve shows the presence of a second absorption band partly hidden by a series of electronic lines. The distance of this band from the principal band is, however, much greater than 7600 cm.$^{-1}$ and probably corresponds to another state of excitation of iodine atoms or of CH_3.

The absorption spectrum of gaseous HI has recently been studied by Goodeve and Taylor.[10] They did not observe two bands, but from the flatness of the maximum of their curve they concluded that the band is double. Furthermore, their curve which is rather similar to ours in the region of long wave-length (a little more steep), tends clearly towards the point corresponding to a dissociation into normal hydrogen and iodine atoms. The absorption curve of CH_3I seems also to tend towards the point corresponding to a dissociation into (in this case) CH_3 and normal iodine atoms, but because of the uncertainty in the calculation of the energy of dissociation of methyl iodide, due to the uncertainty of the energy of the CH bond (106 ± 10 K. cals. according to Penney[11]) no certain conclusion as to the products can be made.

Goodeve and Taylor have calculated a portion of the upper potential energy curve for HI, from the proper functions of the zero point state, by making a series of approximations. In the case of CH_3I the same simplifications cannot be made, as several vibration levels are active and the slope of the upper curve is much less steep than that for HI. Calculations of this curve for methyl and other iodides will, it is hoped, form the subject of a further communication. These calculations will be based on an evaluation of the proper functions for the excited as well as for the normal states.

One of us (D. P.) wishes to express his thanks to the Swiss Ramsay Committee and the Ramsay Memorial Fellowship Trustees for the award of a Fellowship.

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[10] *Proc. Roy. Soc., A,* 1936, **154,** 181.

[11] *Trans. Faraday Soc.,* 1935, **31,** 734.

"THE COMPRESSIBILITY OF LIQUIDS AND A METHOD OF OBTAINING THE COMPRESSIBILITY OF MOLECULES."

By D. B. Macleod, M.A., D.Sc.

Received 19th January, 1937.

Many equations of state have been proposed. As van der Waals' equation undoubtedly represents in a general way the actual behaviour of a fluid, these equations are, for the most part, modifications of van der Waals' equation. They are generally applied down to and in the neighbourhood of the critical temperature.

The work of Bridgman[1] has enormously increased our knowledge of the behaviour of liquids under pressure. The experimental data used in this paper has been taken from this book.

The difficulty of applying van der Waals' equation $\left(p+\frac{a}{v^2}\right)(v-b)=RT$ to a liquid, lies in the fact that the quantities a and b have to be obtained over the comparatively small range of pressure in the neighbourhood of the critical temperature. In the liquid, b becomes the major portion of the total volume. Under the considerable internal pressures of the liquid or under the still greater pressures applied by Bridgman, it becomes impossible to predict the changes in b by deductions made from a study of the liquid under highly expanded conditions. An accurate method of obtaining $(v - b)$, the free space, under actual liquid conditions would remove this uncertainty.

The author has shown in earlier papers, [2, 3, 4], that many problems in connection with the viscosity of a liquid can be discussed satisfactorily on the assumption that the viscosity of a liquid is a simple function of the free space. It is now proposed to show that this free space—calculated from a knowledge of the viscosity and the specific volume of a liquid at two temperatures—can be used to obtain a value of the internal pressure of the liquid. With the aid of a modified van der Waals' equation, the changes in the volume of a liquid with pressure and temperature, can then be traced accurately over a great range of pressure and temperature.

Though the specific volume of a liquid, when plotted against the pressure, lies on a smooth curve, Bridgman[5] shows that, at least, four arbitrary constants are necessary to give a satisfactory relation between volume and pressure. It is proposed to show, by the analysis of this paper, that a satisfactory relation can be obtained with three arbitrary constants, to each of which a definite physical meaning can be assigned.

The Internal Pressure of a Liquid.

The vapour pressure of a liquid at ordinary temperature can be neglected when compared with the internal pressure. The latter, represented by $\frac{a}{V^2}$ or π can, therefore, be written

$$\pi_0 = \frac{RT_0\rho_0}{(v_0 - b)M},$$

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[1] *The Physics of High Pressure.*
[2] *Trans. Faraday Soc.*, 1923, 19.
[3] *Ibid.*, 1925, 21.
[4] *Ibid.*, 1924, 20.
[5] *Loc. cit.*, p. 131.

where R refers to a gram molecule, M is the molecular weight, ρ_0 the density at 0° C., T_0 the absolute temperature and $v_0 - b$ the free space in 1 c.c. of the liquid at 0° C. In this paper, the pressures are expressed in Kg/cm.^{2}. At a temperature T, ρ_0 becomes $\frac{\rho_0}{v_t}$ and the free space in 1 c.c. becomes $\frac{v_t - b}{v_t}$, so that

$$\pi_t = \pi_0 \cdot \frac{v_0 - b}{v_t - b} \cdot \frac{T}{T_0},$$

$(v - b)$, for a liquid, increases more rapidly than the absolute temperature; π_t decreases, therefore, as the temperature is raised.

The values of the free space used in this paper are those given previously,[3] with the necessary correction for temperature.

The internal pressures of the liquid at constant temperature and decreasing volume, following increased external pressure, are assumed to change, following van der Waals, according to the law

$$\pi_p = \pi_0\Big(\frac{v_0}{v_p}$$

The author recently [6].discussed the internal pressure of a liquid and proposed an equation of the type $\pi = Be^{\frac{c}{Tv}}$ for the change of internal pressure with temperature and volume. At constant temperature the results obtained by this equation and by the equation $\pi_p = \pi_0\left(\frac{v_0}{v_p}\right)^2$ are very similar. Substituting, for N. Pentane, in the equation $\pi_0 = \frac{RT_0\rho_0}{(v_0 - b)M}$ the values $M = 72$, $\rho_0 = 0{\cdot}647$, $v_0 - b = 0{\cdot}1220$ (*loc. cit.*)^2 we obtain $\pi_0 = 1690$ Kg./cm.^{2}. Also $v_{50} = 1{\cdot}0837$ and $v_{95} = 1{\cdot}1869$, from which $\pi_{50} = 1186$ and $\pi_{95} = 900$, assuming b to be constant.

On equating $Be^{\overline{T_0 v_0}}$ to 1690 and $Be^{\overline{T_{50} v_{50}}}$ to 1186, the values of B and c are 337·5 and 439·8 respectively.

These constants give $\pi_{95} = Be^{\frac{c}{T_{95} v_{95}}}$ equal to 923 Kg./cm.^{2}, compared with 900 Kg./cm.^{2} calculated direct from the free space.

Considering the latter temperature is 60° C. above the boiling-point of pentane and no correction has been made for any change in b—a correction which will later be shown to be justified—a difference of 2 per cent. can be considered satisfactory.

In Table I. a comparison is made between the internal pressures at 0° C. calculated from the two equations $\pi_p = \pi_0\left(\frac{v_0}{v_p}\right)^2$ where $\pi_0 = 1690$ and $\pi_p = Be^{\frac{c}{T_0 v_p}}$ where $B = 337{\cdot}5$, $C = 439{\cdot}8$. The experimental values of the external pressures and corresponding volumes are taken from Bridgman.

When the large external pressures are added to the internal pressures, the total pressures—which are used in this paper—are very similar. As van der Waals' expression is much simpler and better known, the internal pressures at constant temperature used in this paper, have been calculated from it.

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[6] *Trans. Faraday Soc.*, 1936, 32.

TABLE I.

P_e Km./cm.².	Vol. obs.	$\pi_p = \pi_0\left(\frac{v_0}{v_p}\right)^2$.	$\pi_p = Be^{\frac{c}{T_0 v_p}}$.
0	1·0000	1690	1690
1,000	·9021	2077	2014
2,000	·8546	2314	2225
3,000	·8229	2495	2390
4,000	·7997	2643	2531
5,000	·7811	2770	2654
6,000	·7647	2890	2775
7,000	·7506	3000	2890
8,000	·7381	3100	2994
9,000	·7281	3190	3085
10,000	·7192	3270	3170

Analysis of the Volume of a Liquid.

The changes in the volume of a liquid with pressure are twofold. (1) The free space, which is assumed to obey Boyles' Law and to vary inversely as the total pressure; (2) a molecular portion which behaves like a solid and to which Hooke's Law is applied. It will, also, be shown that the molecular portion can be treated in a manner similar to the original liquid and interpreted by an expression of the type of van der Waals.

For the purposes of this paper a selection of different types of substance has been made from the data supplied by Bridgman. Unfortunately, a large number of the substances studied by him belong to the group of alcohols, which on account of their departure from the simpler laws which apply to unassociated liquids, are unsuitable for a preliminary paper.

The method of procedure will now be illustrated with carbon bisulphide. The free space² in 1 c.c. of CS_2 at 0° C. is 0·1206. The specific volume of 1 c.c. of CS_2 at 20° C. is 1·0235. The free space at 20° C. is taken to be equal to $0·1206 + 0·0235 = 0·1441$; $\rho_0 = 1·292$ and $M = 76$ so that $\pi_{20} = 2904$ Km./cm.².

In Table II. the first column gives the external pressures, P_e, in Kg./cm.², and the third the observed volumes. The second column represents the total pressure or $P_e + \pi_p$, where $\pi_p = 2904 \times \left(\frac{1·0235}{v_p}\right)^2$. The subsequent values in the fourth column are obtained by the Boyle's Law relationship,

$$(v - b)_p = 0·1441 \times \frac{2904}{P_e + \pi_p}.$$

On subtracting $(v - b)_p$ from the observed volumes we obtain column five, which, it is considered, represents the true volume of the molecules. It will be noticed, that if this is true, there is a considerable reduction in the volume of the molecules with pressures up to 12,000 Kg./cm.² Bridgman definitely subscribes to the view that at these high pressures the molecules themselves are compressed.

To column five, an expression of the type $V_m = V_0 - BP + CP^2$ has been applied. As there is a decrease in volume equal to 15 per cent. of the original volume, it is unreasonable to expect it to be covered accurately by a straight line equation of the type $V_m = V_0 - BP$, though for moderate pressures this expression holds satisfactorily. In this equation P represents the sum of the external and internal pressures, namely $P_e + \pi_p$. V_0 will, therefore, be a measure of the volume of the molecules in 1 c.c. of the original material at 0° C. when under no pressure—that is, in the gaseous condition. B is a measure of the compressibility and C the change of compressibility with pressure.

For CS_2 at 20° C., column six has been calculated from the constants. $V_0 = 0{\cdot}9238$, $B = 0{\cdot}0_41658$, $C = 0{\cdot}0_93385$.

TABLE II.

P_e in Kg./cm.².	Carbon Bisulphide at 20° C.				V_m (calc.).	Diff. Per Cent.
	$P_e + \pi_p$.	Vol. obs.	$(v - b)$.	V_m (obs.).		
0	2,904	1·0235	0·1441	0·8794	0·8785	− 0·1
1,000	4,234	·9586	·0989	·8597	·8597	0·0
2,000	5,533	·9173	·0757	·8416	·8425	+ 0·1
3,000	6,773	·8877	·0618	·8259	·8270	+ 0·1
4,000	7,975	·8647	·0525	·8122	·8131	+ 0·1
5,000	9,157	·8453	·0457	·7996	·7994	0·0
6,000	10,320	·8293	·0405	·7888	·7888	0·0
7,000	11,480	·8147	·0365	·7782	·7781	0·0
8,000	12,620	·8022	·0332	·7690	·7685	− 0·1
9,000	13,750	·7911	·0304	·7607	·7598	− 0·1
10,000	14,880	·7805	·0281	·7524	·7522	0·0
11,000	15,990	·7715	·0262	·7453	·7453	0·0
12,000	17,090	·7638	·0245	·7393	·7393	0·0

It will be conceded that the differences between the observed and calculated columns are practically within the experimental error. This indicates that, on subtracting from the original volume a quantity obeying Boyle's Law, the residuum conforms accurately to the same type of law that represents the change of volume of a solid with pressure.

It might be thought that the same type of analysis could be made with any value of the free space. This is definitely not so. For example, if the value of the free space be taken as 0·1800 instead of 0·1441, a difference representing less than 4 per cent. of the original column, the residuum in column five, instead of decreasing by a smooth curve to which a simple expression can be applied, definitely rises to a maximum for higher pressures and falls again to a value similar to that obtained in the above case. It is obvious that such a change can have no real physical meaning and the analysis fails. In like manner, if the free space is reduced by an amount representing 4 per cent. of the original volume, the column representing the volume of the molecules, gives a complicated curve to which no simple interpretation can be given. The value of the free space that can be used for the analysis of this paper is, therefore, critical. The method of calculation from viscosity leaves room, however, for uncertainties of the order of a few per cent. of the values used, representing, at the outside, possibly 1 per cent. of the original volume of the liquid. The lack of agreement with some substances, especially in the initial value, can almost certainly be explained by a small error in the initial value of the free space. In the whole of the subsequent calculations, a difference between observed and calculated value of the order of 1 per cent., occurs in one reading only and there are few divergences greater than 0·5 per cent. The initial uncertainties in the free space, are not sufficient, therefore, to affect the general accuracy or applicability of the method.

Application of van der Waals' Equation to the Molecule Itself.

It is proposed to assume that within the molecule, the atoms are relatively incompressible compared to the molecule as a whole and that they occupy a limited part of the total volume. There must, also, be a pressure within the molecule resisting compression. This pressure would be, in part, due to repulsive static forces and, in part, to the kinetic properties of the atoms due to temperature. When the molecule is freed from external pressures, this pressure would be equal to the attractive forces holding the molecule together. If we call this static attractive pressure P_m, and regard it as practically constant for the change of volume dealt with in this data, we can say that a liquid molecule is being compressed by a force equal to $P_e + \pi_p + P_m$, where P_e is the external applied pressure, π_p the internal pressure of the liquid and P_m the constant attractive force over the molecule. For equilibrium, the resisting forces within the molecule, namely the repulsive static forces and kinetic forces, must equal the sum of these combined forces. We have, therefore, an analogy with the liquid itself and can write

$$P_e + \pi_p + P_m = \frac{K}{V_m - b_a},$$

where V_m represents the volume of the molecule; b_a the volume of the atoms within the molecule, considered constant; and K a constant for a particular molecule at a constant temperature. There are, here, three unknowns, as in the previous equation, namely, P_m, K and b_a. It will be shown that this equation gives a better agreement with the substances studied in this paper, than the previous one $V_m = V_0 - BP + CP^2$.

In Table III. the agreement, by this equation, between the observed and calculated values, is shown. The values of the constants are $P_m = 18{,}426$ Kg./cm.^{2} $K = 7595$ and $b_a = 0{\cdot}5247$. The experimental errors can hardly be much less than these differences.

Before discussing the significance and importance of the constants

TABLE III.—CS_2 AT 20° C.

P_e in Kg./cm.^{2}	V_m(obs.).	V_m(calc.).	Diff. Per Cent.
0	0·8794	0·8808	+ 0·14
1,000	·8597	·8597	0·00
2,000	·8416	·8416	0·00
3,000	·8259	·8260	0·01
4,000	·8122	·8124	+ 0·02
5,000	·7996	·8001	+ 0·07
6,000	·7888	·7888	0·00
7,000	·7782	·7787	+ 0·07
8,000	·7690	·7693	+ 0·04
9,000	·7607	·7608	0·01
10,000	·7524	·7527	+ 0·04
11,000	·7453	·7453	0·00
12,000	·7393	·7397	+ 0·04

obtained by these two equations, the results obtained with other liquids will be given. In the following table, column six gives the values of

TABLE IV.

P_t in Kg./cms.	$P_t + \pi_p$	Vol. (obs.)	$v - b$.	V_m (obs.).	V_m (1)	Diff. %.	V_m (2).	Diff. %.
N. Pentane at 0° C.*								
0	1,690	1·0000	0·1220	0·8780	0·8722	− 0·7	0·8657	− 1·5
1 000	3,077	·9021	·0670	·8351	·8351	0·0	·8351	0·0
2,000	4,314	·8546	·0477	·8069	·8081	+ 0·2	·8104	+ 0·4
3,000	5,495	·8229	·0375	·7854	·7870	+ 0·2	·7890	+ 0·4
4,000	6·643	·7997	·0310	·7687	·7694	+ 0·1	·7706	+ 0·3
5,000	7,770	·7811	·0265	·7546	·7546	0·0	·7546	0·0
6,000	8,890	·7647	·0232	·7415	·7412	0·0	·7411	− 0·1
7,000	10,000	·7506	·0206	·7300	·7301	0·0	·7287	− 0·2
8,000	11,100	·7381	·0186	·7195	·7200	+ 0·1	·7190	− 0·1
9,000	12,190	·7281	·0169	·7112	·7112	0·0	·7111	0·0
10,000	13,270	·7192	·0156	·7036	·7031	− 0·1	·7054	+ 0·2
Ether at 20° C.								
0	1,580	1·0315	0·1549	0·8766	0·8812	+ 0·6	0·8734	− 0·4
1,000	2,917	·9363	·0839	·8524	·8502	− 0·2	·8488	− 0·4
2,000	4,136	·8871	·0592	·8279	·8266	− 0·2	·8279	0·0
3,000	5,310	·8530	·0461	·8069	·8069	0·0	·8092	+ 0·3
4,000	6,454	·8275	·0379	·7896	·7902	+ 0·1	·7922	+ 0·3
5,000	7,580	·8071	·0323	·7748	·7755	+ 0·1	·7771	+ 0·3
6,000	8,683	·7916	·0282	·7634	·7627	− 0·1	·7634	0·0
7,000	9,782	·7773	·0250	·7523	·7512	− 0·2	·7509	− 0·2
8,000	10,875	·7645	·0225	·7420	·7410	− 0·1	·7400	− 0·3
9,000	11,970	·7525	·0204	·7321	·7316	− 0·1	·7300	− 0·3
10,000	13,054	·7418	·0187	·7231	·7231	0·0	·7215	− 0·2
11,000	14·144	·7312	·0173	·7139	·7153	+ 0·2	·7139	0·0
12,000	15,227	·7216	·0161	·7055	·7081	+ 0·4	·7079	+ 0·4
Ethyl Iodide at 20° C.								
0	2,787	1·0214	0·1121	0·9093	0·9060	− 0·3	0·9014	+ 0·2
1,000	4,216	·9509	·0741	·8768	·8768	0·0	·8768	0·0
2,000	5,525	·9092	·0565	·8527	·8540	+ 0·1	·8558	+ 0·4
3,000	6,753	·8802	·0463	·8339	·8356	+ 0·2	·8375	+ 0·4
4,000	7,946	·8583	·0393	·8190	·8196	+ 0·1	·8212	+ 0·3
5,000	9,126	·8394	·0342	·8052	·8056	+ 0·1	·8064	+ 0·1
6,000	10,287	·8236	·0304	·7932	·7932	0·0	·7932	0·0
7,000	11,440	·8093	·0273	·7820	·7820	0·0	·7813	− 0·1
8,000	12,580	·7968	·0248	·7720	·7720	0·0	·7708	− 0·2
9,000	13,710	·7856	·0228	·7628	·7629	0·0	·7616	− 0·2
10,000	14,835	·7755	·0210	·7545	·7544	0·0	·7535	− 0·1
11,000	15,950	·7665	·0196	·7469	·7468	0·0	·7469	0·0
12,000	17,050	·7588	·0183	·7405	·7400	− 0·1	·7413	+ 0·1
Mercury at 0° C.†								
0	35,300	1·0000	0·0443	0·9557	0·9557	0·0		
1,000	36,560	·9963	·0428	·9535	·9535	0·0		
2,000	37,820	·9926	·0413	·9513	·9513	0·0		
3,000	39,090	·9891	·0400	·9491	·9491	0·0		
4,000	40,360	·9856	·0388	·9468	·9469	0·0		
5,000	41,590	·9823	·0376	·9447	·9447	0·0		
6,000	42,830	·9781	·0365	·9426	·9426	0·0		
7,000	44,070	·9760	·0355	·9405	·9404	0·0		

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† Column six for Mercury is calculated from the simpler expression $V_m = V_0 - BP$, where $V_0 = 1{\cdot}0170$ and $B = 0{\cdot}0_5 1738$.
The other type of expression is inapplicable to mercury.

TABLE IV.—*continued*

CONSTANTS.

1.			2.		
b_a.	K.	P_m.	V_0.	B.	C.
0·5451	3542	9143	0·9073	$0 \cdot 0_4 2596$	$0 \cdot 0_9 8104$
0·5350	4727	12,070	0·9049	$0 \cdot 0_4 2075$	$0 \cdot 0_9 513$
0·5570	5486	12,940	0·9553	$0 \cdot 0_4 2065$	$0 \cdot 0_9 4755$

V_m calculated from the expression $P_e + \pi_p + P_m = \frac{K}{V_m - b_a}$ and column seven from the expression $V_m = V_0 - BP + CP^2$.

Discussion of Results at Lower Temperatures.

Before proceeding to a discussion of the constants, it is possible to show the general accuracy of the free space and internal pressures obtained, by calculating up to the critical temperature. Thus for mercury at 0° C., the free space is 0·0443 and the internal pressure 35,300 Kg./cm.^{2}. The critical temperature of mercury is taken as 1450° C. and the critical pressure 1040 Kg./cm.^{2}. By van der Waals' equation the total pressure (internal and external) at the critical temperature is four times the critical pressure. The volume of the free space at the critical temperature, should, therefore, be $0 \cdot 0443 \times \frac{35300}{4 \times 1040} \times \frac{1723}{273} = 2 \cdot 37$. The volume of the corresponding molecular portion is 1·02. The total volume at the critical temperature becomes 3·39. The volume occupied by the molecular portion at the critical temperature approximates very closely to the value 1/3 required by van der Waals' equation.

The corresponding quantities for CS_2 at 20° C. are

$$0 \cdot 1441 \times \frac{2904}{4 \times 72 \cdot 9} \times \frac{546}{293} = 2 \cdot 66,$$

where $p_c = 72 \cdot 9$ Kg./cm.^{2} and $\theta_c = 273°$ C.

Ether $p_c = 36 \cdot 0$ Kg./cm.^{2} and $\theta_c = 197°$ C. gives

$$0 \cdot 1549 \times \frac{1580}{4 \times 36 \cdot 0} \times \frac{470}{293} = 2 \cdot 72,$$

and Pentane $p_c = 33 \cdot 1$ Kg./cm.^{2} and $\theta_c = 197°$ C.

$$0 \cdot 1220 \times \frac{1690}{4 \times 33 \cdot 1} \times \frac{470}{293} = 2 \cdot 50.$$

The critical pressure of ethyl iodide is not available.

Considering the totally different internal pressures of the three organic liquids from that of mercury and the fact that, for mercury, the extrapolation is from 0° C. to 1500° C., the constancy of these quantities is satisfactory and is of the order required by van der Waals' equation.

The internal pressures of the various liquids vary from 35,000 Kg./cm.^{2} for mercury at 0° C. to 1580 Kg./cm.^{2} for ether at 20° C. The values obtained are of the order of the usually accepted ones.[7] Richards[8] from other considerations, arrives at a value for mercury very similar to that calculated in this paper.

From the relation $v_m = V_0 - BP + CP^2$, the compressibility $\frac{1}{V_0} \cdot \frac{dv}{dp} = B - 2\,CP$. For the mercury atom at 0° this has a value approximately $0{\cdot}0_5 17$ per megabar. It might be expected that the compressibility of the mercury atom would correspond to the same order as that of a solid, say gold which is $0{\cdot}5 \times 10^{-6}$ per megabar. It has been shown by Richards[8] that the internal pressure in solid gold is of the order of 300,000 atmospheres. The atoms of gold are, therefore, under a pressure of the order of ten times that of the mercury atom in the liquid and the compressibility of the gold atom has been, thereby, greatly reduced. The same considerations apply in comparing the compressibility of the organic substances in the liquid form with the same type of material in the solid form. The internal forces in solids are very much greater than in liquids and the molecular compressibility correspondingly reduced.

The values of V_0, B and C for the liquids under consideration are as in Table V.

TABLE V.

	V_0.	B.	C.
Mercury . . .	1·0170	$0{\cdot}0_5 1738$	—
Carbon bisulphide .	·9238	$0{\cdot}0_4 1658$	$0{\cdot}0_9 3385$
Ethyl iodide . .	·9553	$0{\cdot}0_4 2065$	$0{\cdot}0_9 4755$
Ether . . .	·9049	$0{\cdot}0_4 2075$	$0{\cdot}0_9 513$
N. pentane . .	·9073	$0{\cdot}0_4 2596$	$0{\cdot}0_9 8104$

As already pointed out, V_0 represents the volume of the molecules in 1 c.c. of the liquid at 0° C., when released from all external pressures. In the case of mercury the value is greater than unity partly because only a very small fraction of the total volume in the liquid is free space and also because the atoms in the liquid under ordinary conditions are under a great compressive force due to its high internal pressure. When this pressure is removed by vaporising the liquid, the volume of the atoms increases from 0·956 to 1·017 or practically 6 per cent. The value of V_0 for the various liquids depends, of course, on the extent to which the liquid has been expanded at the considered temperature or in other words, to the proximity of the temperature of reference to the boiling-point of the liquid. The values of V_0 are in the same order as the boiling-points. The increase of the molecular volume of the organic substances on being vaporised is of the order of 4 per cent., which is the correction necessary to b of van der Waals' equation, in passing from the vapour to the ordinary liquid condition.

The values of B and C, depend, probably, on the complexity of the molecules, being least for mercury and definitely smaller for CS_2 than for ether and pentane. B and C (the compressibility and the change of compressibility with pressure) increase together as might be expected.

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[7] Compare Lewis, " A System of Physical Chemistry," page 103, ethyl ether, 1300 atmos., CS_2 2900 atmos. at 0° C.

[8] *J. Amer. Chem. Soc.*, 1926, 48, 3063.

The constants, P_m, K, and b_a for the organic liquids are given in Table VI.

TABLE VI.

	P_m.	K.	b_a
Carbon bisulphide .	18,420	7595	0·5247
Ethyl iodide . .	12,040	5486	0·5570
Ether . . .	12,070	4727	0·5350
Pentane . . .	9,143	3542	0·5451

It will be noticed that the proportion of the molecule occupied by the atoms, b_a, is practically the same for the various molecules considered and is from 50 per cent. to 60 per cent. of the total volume. That means that the molecule is actually a more open structure than the liquid itself, though, of course, the "free space" within the molecule is the seat of much greater forces than the "free space" of the liquid and, therefore, less compressible.

P_m can be considered to represent the stress within the molecule itself. It has been taken to be a constant over the range of change of volume in these measurements, though this must, obviously, be only approximately true. It decreases from 18,000 Kg./cm.^{2} for CS_2 to 9000 Kg./cm.^{2} for pentane. It is difficult to say whether the values obtained for P_m and b_a are of the order to be expected as the author is not aware, that the molecule has been treated from this point of view previously. P_m would represent the mean resistance to compression of the molecule when considered over a sphere. The resistance along the valency bonds would probably exceed this mean value. P_m should also be related to the temperature required to dissociate the molecule in the same way as the internal pressure of a liquid is related to its boiling-point.

The values of K for the various substances can best be compared by calculating them for a gram molecule. The results for carbon bisulphide, ethyl iodide and ether at 20° C. are $4{\cdot}47 \times 10^5$, $4{\cdot}37 \times 10^5$, $4{\cdot}80 \times 10^5$ and for pentane at 0° C. $3{\cdot}92 \times 10^5$. Considering the elements of uncertainty in calculating the constants, it might prove that K will be practically a constant for a wide range of substances, when referred to a gram molecule.

Results at Higher Temperatures.

Bridgman gives the compressibilities of carbon bisulphide, ethyl iodide and ether at 80° C., and of pentane at 50° C. and 95° C. These temperatures are well above the boiling-points of the liquids and data is not available to calculate the free space from the viscosity data direct. It can, however, be obtained from the change of volume and it is possible from the, now known, change of volume of b with pressure to apply a correction for the reduction of internal pressure at the higher temperature.

The method can be illustrated with pentane. At 0° C. the free space for pentane has been taken as 0·1220. The volume of 1 c.c. at 0° C. when raised to 50° C. is 1·0837. If b were constant the free space at 50° C. would be $0{\cdot}1220 + 0{\cdot}0837 = 0{\cdot}2057$. Using the expression

$$\pi_{50} = \pi_0 \cdot \frac{v_0 - b}{v_{50} - b} \cdot \frac{T_{50}}{T_0}$$

this would give $\pi_{50} = 1186$, where $\pi_0 = 1690$. This means a reduction of approximately 500 Kg./cm.² in the internal pressure. The value of B, given earlier in the paper, for pentane is $0{\cdot}0_4 26$. The change due to C is negligible over this range of pressure. The change in the volume of the molecular portion to a first approximation is, therefore, $0{\cdot}0_4 26 \times 500 = 0{\cdot}0130$.

A series of such approximations leads to a final value for the change of the molecular volume as 0·0110. V_m at 0° C. has been given as 0·8780. V_m at 50° C. is, therefore, 0·8890. The total volume at 50° C. is 1·0387, which leaves the initial value of the free space as 0·1947, from which the internal pressure can be calculated. As the free space occupies only a small fraction of the total volume, a small percentage change in the molecular portion means a much larger percentage change in the free space.

Table VII. gives the results for the various liquids calculated at higher temperatures. In calculating the constants from the equation

$$P_e + \pi_p + P_m = \frac{K}{V_m - b_a},$$

TABLE VII.

P_e.	$P_e + \pi_p$.	Vol. (obs.).	$V - b$.	V_m (obs.).	V_m (1).	Diff. Per Cent.	V_m (2).	Diff. Per Cent.
Pentane at 50° C.								
0	1,260	1·0837	0·1947	0·8890	0·8862	− 0·3	0·8794	− 1·0
1,000	2,676	·9395	·0917	·8472	·8472	0·0	·8472	0·0
2,000	3,902	·8820	·0629	·8191	·8200	+ 0·1	·8221	+ 0·4
3,000	5,070	·8454	·0484	·7970	·7983	+ 0·2	·8005	+ 0·4
4,000	6,204	·8193	·0395	·7798	·7802	+ 0·1	·7816	+ 0·2
5,000	7,320	·7985	·0335	·7650	·7649	0·0	·7650	0·0
6,000	8,430	·7807	·0291	·7516	·7514	0·0	·7507	− 0·1
7,000	9,525	·7657	·0258	·7399	·7396	0·0	·7384	− 0·2
8,000	10,620	·7520	·0231	·7289	·7292	0·0	·7281	− 0·1
9,000	11,695	·7409	·0210	·7199	·7199	0·0	·7199	0·0
10,000	12,765	·7316	·0192	·7124	·7116	− 0·1	·7136	+ 0·2
Pentane at 95° C.								
0	956	1·1869	0·2907	0·8962	0·9017	+ 0·6	0·8984	+ 0·3
1,000	2,412	·9768	·1150	·8598	·8598	0·0	·8618	+ 0·3
2,000	3,635	·9078	·0764	·8314	·8314	0·0	·8342	+ 0·3
3,000	4,790	·8671	·0580	·8091	·8089	0·0	·8110	+ 0·2
4,000	5,922	·8371	·0469	·7902	·7900	0·0	·7906	+ 0·1
5,000	7,040	·8125	·0395	·7730	·7741	+ 0·1	·7730	0·0
6,000	8,140	·7933	·0341	·7592	·7600	+ 0·1	·7582	− 0·1
7,000	9,230	·7775	·0301	·7474	·7478	0·0	·7457	− 0·2
8,000	10,310	·7641	·0270	·7371	·7370	0·0	·7358	− 0·2
9,000	11,380	·7527	·0244	·7283	·7277	− 0·1	·7283	0·0
10,000	12,440	·7433	·0223	·7210	·7190	− 0·3	·7228	+ 0·2
Carbon Bisulphide at 80° C.								
0	2,294	1·1092	0·2198	0·8894	0·8987	+ 1·0	0·8979	+ 1·0
1,000	3,777	1·0083	·1335	·8748	·8748	0·0	·8748	0·0
2,000	5,093	·9552	·0990	·8562	·8562	0·0	·8560	0·0
3,000	6,347	·9185	·0794	·8391	·8398	+ 0·1	·8393	0·0
4,000	7,562	·8902	·0667	·8235	·8257	+ 0·3	·8245	+ 0·1
5,000	8,750	·8676	·0576	·8100	·8129	+ 0·3	·8112	+ 0·1
6,000	9,905	·8501	·0509	·7992	·8017	+ 0·3	·7992	0·0
7,000	11,050	·8347	·0456	·7891	·7912	+ 0·2	·7890	0·0
8,000	12,177	·8220	·0414	·7806	·7817	+ 0·1	·7790	− 0·1
9,000	13,290	·8107	·0379	·7728	·7728	0·0	·7707	− 0·3
10,000	14,410	·7997	·0349	·7648	·7648	0·0	·7634	− 0·2
11,000	15,520	·7894	·0325	·7569	·7571	0·0	·7571	0·0
12,000	16,645	·7795	·0303	·7492	·7498	+ 0·1	·7517	+ 0·3

TABLE VII.—*continued.*

P_e.	$P_e + \pi_p$.	Vol. (obs.).	$V - b$.	V_m (obs.).	V_m (1).	Diff. Per Cent.	V_m (2).	Diff. Per Cent.
Ether at 80° C.								
0	—	—	—	—	—	—	—	—
1,000	2,330	0·9906	0·1266	0·8640	0·8688	+ 0·6	0·8650	+ 0·1
2,000	3,690	·9223	·0800	·8423	·8424	0·0	·8423	0·0
3,000	4,944	·8812	·0597	·8215	·8215	0·0	·8228	+ 0·2
4,000	6,154	·8515	·0479	·8036	·8040	+ 0·1	·8054	+ 0·2
5,000	7,328	·8289	·0403	·7886	·7890	0·0	·7899	+ 0·2
6,000	8,475	·8112	·0348	·7764	·7757	− 0·1	·7762	0·0
7,000	9,613	·7953	·0307	·7646	·7640	− 0·1	·7640	− 0·1
8,000	10,740	·7813	·0275	·7538	·7532	− 0·1	·7528	− 0·1
9,000	11,870	·7687	·0249	·7438	·7434	− 0·1	·7428	− 0·1
10,000	12,990	·7574	·0227	·7347	·7348	0·0	·7345	0·0
11,000	14,100	·7469	·0209	·7260	·7268	+ 0·1	·7273	+ 0·2
12,000	15,210	·7365	·0193	·7173	·7193	+ 0·3	·7212	+ 0·5
Ethyl Iodide at 80° C.								
0	2,090	1·0935	0·1800	0·9135	·09158	+ 0·2	0·9129	− 0·1
1,000	3,510	·9969	·1072	·8897	·8870	− 0·3	·8869	− 0·3
2,000	4,810	·9425	·0782	·8643	·8643	0·0	·8641	0·0
3,000	6,040	·9065	·0623	·8442	·8458	+ 0·2	·8463	+ 0·3
4,000	7,230	·8790	·0520	·8270	·8296	+ 0·3	·8295	+ 0·3
5,000	8,390	·8581	·0448	·8133	·8155	+ 0·3	·8151	+ 0·2
6,000	9,530	·8418	·0395	·8023	·8030	+ 0·1	·8016	− 0·1
7,000	10,660	·8264	·0353	·7911	·7917	+ 0·1	·7900	− 0·1
8,000	11,780	·8134	·0327	·7807	·7803	0·0	·7798	− 0·1
9,000	12,890	·8013	·0292	·7721	·7725	+ 0·1	·7711	− 0·1
10,000	14,000	·7909	·0269	·7640	·7640	0·0	·7638	0·0
11,000	15,090	·7817	·0249	·7568	·7563	− 0·1	·7579	+ 0·2
12,000	16,180	·7737	·0233	·7504	·7492	− 0·2	·7533	+ 0·4
Mercury at 20° C.								
0	35,190	1·0036	0·0477	0·9559	0·9560	0·0		
1,000	36,460	·9997	·0460	·9537	·9536	0·0		
2,000	37,720	·9959	·0445	·9514	·9514	0·0		
3,000	39,010	·9923	·0430	·9493	·9492	0·0		
4,000	40,220	·9888	·0417	·9471	·9471	0·0		
5,000	41,490	·9854	·0405	·9449	·9449	0·0		
6,000	42,720	·9822	·0393	·9429	·9429	0·0		
7,000	43,970	·9790	·0382	·9408	·9409	0·0		
8,000	45,210	·9761	·0371	·9390	·9390	0·0		
9,000	46,410	·9733	·0362	·9371	·9371	0·0		
10,000	47,600	·9706	·0353	·9353	·9353	0·0		
11,000	48,810	·9681	·0344	·9337	·9335	0·0		
12,000	50,000	·9657	·0336	·9321	·9318	0·0		

Constants.*

1.			2.		
b_a.	K.	P_m.	V_0.	B.	C.
0·5450	3744	9714	0·9107	$0{\cdot}0_{4}2588$	$0{\cdot}0_{9}8181$
0·5450	3894	9965	0·9248	$0{\cdot}0_{4}2849$	$0{\cdot}0_{9}9840$
0·5247	8116	19,400	0·9369	$0{\cdot}0_{4}1798$	$0{\cdot}0_{9}4123$
0·5350	5302	13,556	0·9084	$0{\cdot}0_{4}1973$	$0{\cdot}0_{9}4886$
0·5570	5828	14,150	0·9550	$0{\cdot}0_{4}214$	$0{\cdot}0_{9}546$
			1·0386	$0{\cdot}0_{5}2852$	$0{\cdot}0_{10}1432$

the value of b_a for a given substance is taken to be the same as that at the lower temperature. There are, therefore, at the higher temperatures only two arbitrary constants used in calculating column six V_m (1), namely, P_m and K. The percentage errors might, therefore, be expected to be greater. A comparison of the figures show that they are similar to those at the lower temperatures and smaller than those from the equation $V_m = V_0 - BP + CP^2$.

These same constants cover accurately the values for mercury at 0° C. Bridgman[9] draws attention to ratio of $2C/B$ for solids being of the order of 10^{-5} for the metallic elements. He points out that reciprocal of this quantity, namely, 10^5 has the dimensions of pressure and 10^5 Kg./cm.^{2} is of the order of the pressure which would be exerted by the various metals if the atoms were completely disintegrated into a gas of electrons and protons, acting according to classical gas laws, and occupying the actual volume of the metal. It is noticeable that $2C/B$ is, in this case, exactly 10^{-5}.

The coefficients V_0, B and C at the different temperatures are tabulated in Table VIII.

TABLE VIII.

		V_0.	B.	C.
Mercury . . .	20° C.	1·0170	$0{\cdot}0_5 1738$	—
	80° C.	1·0386	$\cdot 0_5 2852$	$0{\cdot}0_{10} 1432$
Carbon bisulphide .	20° C.	·9238	$\cdot 0_4 1658$	$\cdot 0_9 3385$
	80° C.	·9369	$\cdot 0_4 1798$	$\cdot 0_9 4123$
Ethyl iodide . .	20° C.	·9553	$\cdot 0_4 2065$	$\cdot 0_9 4755$
	80° C.	·9550	$\cdot 0_4 2140$	$\cdot 0_9 5460$
Ether . . .	20° C.	·9049	$\cdot 0_4 2075$	$\cdot 0_9 513$
	80° C.	·9084	$\cdot 0_4 1973$	$\cdot 0_9 4886$
Pentane . . .	0°	·9073	$\cdot 0_4 2596$	$\cdot 0_9 8104$
	50°	·9107	$\cdot 0_4 2588$	$\cdot 0_9 8181$
	95°	·9248	$\cdot 0_4 2849$	$\cdot 0_9 9840$

While too much reliance must not be placed on the exact values of the coefficients, as they are dependent on the particular experimental values from which they are calculated, they are evidently characteristic of the substance. The general increase of V_0 with rise of temperature would indicate that the molecule itself expands with rise of temperature as it does with decreasing pressure, a result to be expected. At the same time, the slightly larger values of B and C indicate that it becomes more compressible, behaving in these respects, as a liquid. It is, perhaps, significant that, whereas the internal pressures of the molecules are of the order of ten times the internal pressures of the liquids, the compressibilities of the molecules are of the order of one-tenth of those of the liquids. It is significant that though the free space at the higher temperature is in the case of pentane two and a half times that at the lower temperature, the coefficients of the molecular portion remain practically constant. The same remark applies to the other liquids.

Table IX. sets out the constants K, P_m and b_a for the various substances at different temperatures.

It will be remembered, that in obtaining the molecular volume at the higher temperature, allowance was made for the previously determined change of volume with pressure. No correction was made for

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[9] *Loc. cit.*,[1] p. 170.

TABLE IX.

	Temp. °C.	P_m.	K.	b_a.
Carbon bisulphide .	20	18,426	7,595	0·5247
	80	19,400	8,116	·5247
Ethyl iodide . .	20	12,940	5,486	·5570
	80	14,150	5,828	·5570
Ether . . .	20	12,070	4,727	·5350
	80	13,556	5·302	·5350
Pentane . . .	0	9,143	3,542	·5451
	50	9,714	3,744	·5451
	95	9,965	3,894	·5451

a possible increase of volume with temperature. The above constants are calculated, therefore, at constant volume as far as temperature is concerned. Under such circumstances an increase of the internal pressure of the molecule with rise of temperature is to be expected. The forces within the molecule are largely static, the kinetic forces due to the vibrations of the atoms, being, at temperatures far removed from the temperature of dissociation, probably relatively small. It is not, therefore, to be expected that P_m would bear any simple relationship to the absolute temperature. This is further emphasised by the small change of K with temperature. On the strict analogy with a fluid K should be equivalent to RT. If K were dependent on static forces alone, it would probably be independent of temperature. As the temperature of dissociation of the molecule is approached, the importance of the kinetic forces would probably increase and K become more dependent on the absolute temperature. We might write $K = a + bT$, the stability of the molecule being dependent on the relative values of a and bT.

Further work is necessary to establish the constants and to compare them for various classes of substances.

General Discussion.

Many points discussed by Bridgman in connection with liquids can be answered satisfactorily from this analysis. For example he shows[10] that if a liquid con be represented by an equation of the type $P = Tf_1(v) + f_2(v)$ then $\left(\frac{dp}{dT}\right)_v = f(v)$ and $\frac{p_3 - p_2}{p_2 - p_1}$ should equal $\frac{T_3 - T_2}{T_2 - T_1}$. He finds, however, that this relationship does not hold with actual liquids.

In the first place, p_1, p_2 and p_3, from the point of view of this paper, should not be the external pressures, but the true internal pressures. It has been shown by the above analysis, that $f_2(v)$ which refers to the molecular portion, is itself a function of temperature. It is, therefore, not to be expected that $\frac{p_2 - p_2}{p_2 - p_1}$ should equal $\frac{T_3 - T_2}{T_2 - T_1}$. The agreement can, however, be shown to be better if the total pressure $P_e + \pi_p$ is substituted for the external pressures P_e.

Bridgman[11] also discusses the fact that $\left(\frac{d^2v}{dT^2}\right)_p > 0$ at low pressures but becomes negative at high pressures. At low external pressures the internal pressures are decreasing rapidly as the temperature is raised, with constant external pressures and the liquid is largely obeying Boyle's Law. At high pressures, the internal pressures are almost constant at various temperatures with constant external pressures and the liquid is confirming to Hooke's Law. The changes taking place are analysed by the equations developed in this paper.

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[10] *Loc. cit.*,[1] p. 138.

[11] *Ibid.*, p. 136.

Summary.

The volume of a liquid under pressure can be represented with considerable accuracy by one or other of the following equations:

$$(a)\ V_p = \frac{\pi_0(v_0 - b)}{P_e + \pi_p} + V_0 - B(P_e + \pi_p) + C(P_e + \pi_p)^2$$

where P_e = external pressure, $v_0 - b$ = the free space. In this paper $v_0 - b$ has been calculated from data independent of that to which it is subsequently applied—namely from viscosity data.

$$\pi_0 = \frac{RT_0}{v_0 - b},$$

and

$$\pi_p = \pi_0 (-$$

Where v_0 and v_p are the experimental volumes. V_0 = the volume of the molecules in 1 c.c. of the substance at 0° C. when in the gaseous condition and B and C are constants proportional to the compressibility of the molecules and to the change of compressibility with pressure respectively.

$$(b)\ V_p = \frac{\pi_0(v_0 - b)}{P_e + \pi_p} + \frac{K}{P_e + \pi_p + P_m} + b_a,$$

where P_m = the internal pressure of a molecule,
b_a = the volume of the atoms in the molecule,
K = a constant for a particular molecule at a constant temperature.
If applied to a gram molecule, the value of K does not vary markedly for different organic substances. In each of these equations there are three arbitrary constants, to each of which a definite physical meaning has been attached. Of these two equations, the latter gives the better agreement between observed and calculated values.

In conclusion, I wish to express my thanks to Dr. C. Coleridge Farr, F.R.S., for his continued help and encouragement in this work, and also to Mr. C. J. Banwell, M.Sc., for many helpful discussions and suggestions. I wish also to thank Professor E. K. Rideal, F.R.S., for his kindness in accepting the responsibility of sponsoring my papers.

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THE ELECTRIC CHARGE AT AN OIL-WATER INTERFACE.

By W. C. M. Lewis.

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At an interface such as that of oil in contact with water (or an aqueous solution) there exists in general a potential difference associated with the formation of an electrical double layer. In order that such a distribution of electric charge may be possible, there must exist within the double layer a mechanical pressure preventing the collapse of the layer. In the case of a plane parallel plate condenser the magnitude of this pressure is given by the expression $2\pi\sigma^2/K$ where K is the dielectric capacity and σ the surface charge density.

It is now usual to regard the composite double layer as made up of two parts, one, of the Helmholtz type wherein the charges on the oil surface (surface charge density σ) are faced by charges of opposite sign thereto, the distance of separation δ_0 being that of a unimolecular layer of water, *i.e.* $\delta_0 = 3 \times 10^{-8}$ cm. approximately. The balancing charges located in the water in the above case are so tightly bound that they are not regarded as playing any part in electrokinetic phenomena. The greater part of the total charge upon the oil is regarded as balanced by these firmly held ions. In addition to the " rigid " Helmholtz double layer there is likewise a diffuse layer in which there is an excess of ions of sign opposite to those primarily adsorbed upon the oil surface itself and completing the balancing effect necessary to render the entire interfacial layer electrically neutral. The ions of the diffuse layer being mobile are regarded as being responsible for all electro-kinetic phenomena. The number of excess ions (of sign opposite to that on the oil) is small compared with the number of balancing ions which form the " water " side of the Helmholtz layer itself. Further, when sufficient concentration c of electrolyte is present in the aqueous solution, the diffuse layer—the thickness of which varies as $1/\sqrt{c}$—can be reduced to zero, under which condition the charge density upon the oil itself presumably attains an upper limit σ_0, if it has not already done so.

Since we are regarding the total interfacial layer as divisible into two parts, there will likewise be in principle two pressure terms, namely, (*a*) that obtaining in the Helmholtz layer in which the pressure may attain a very high value owing to the magnitude of σ, and (*b*) that obtaining in the outer diffuse layer in which the pressure would be expected to be much lower as its magnitude is determined by σ_{ek} the electrokinetic charge density expressed in terms of surface charge density.

Calculation of the Maximum Total Charge Density (σ_0) upon the Oil Surface.

The upper limit of σ, namely σ_0, is likely to be reached when sufficient electrolyte has been added to " close down " the diffuse layer completely. Under these circumstances the electrical distribution corresponds with that of the Helmholtz layer of thickness δ_0, the opposite charges being separated by a unimolecular layer of water ($\delta_0 = 3 \times 10^{-8}$ cm. approx.). The energy of this simple double layer condenser is $2\pi\sigma_0{}^2\delta_0/K$. This energy term would be reduced to zero if the " plates " were actually to come together. It is postulated that the " plates " are kept apart by the unimolecular layer of water which adheres firmly to the outermost layer of oil. The energy necessary to remove this water layer would appear to be identical with the energy of adhesion, A, which manifests itself when water and oil are brought into contact. From capillary measurements, A is known to be about 45 ergs per cm.^{2} for the case of water in contact with a saturated hydrocarbon. A *maximum* value for the electrical energy term and consequently for the total charge density would thus be obtained by writing

$$A = 2\pi\sigma_0{}^2\delta_0/K.$$

Whence, in the case considered, $\sigma_0{}^2 = 2{\cdot}4 \times 10^8 K$. Within the oriented unimolecular layer the value to be ascribed to K must be much lower than the normal value for water in bulk. The suggestion has been made that it might be as low as 3. Rideal suggests the somewhat larger value 7.

$$\text{With } K = 3,\ \sigma_0 = 2{\cdot}7 \times 10^4 \text{ e.s.u.}$$
$$\text{With } K = 7,\ \sigma_0 = 4{\cdot}1 \times 10^4 \text{ e.s.u.}$$

Denoting by V the potential difference across the double layer and setting V equal to $4\pi\sigma_0\delta_0/K$, it follows that,

$$\text{With } K = 3,\ V = 1{\cdot}02 \text{ volt.}$$
$$\text{With } K = 7,\ V = 0{\cdot}68 \text{ volt.}$$

Neither of these values is wholly improbable—in the light of the usual estimate of absolute p.d. at electrodes—but of the two, the lower value 0·68 volt would be regarded as the more probable. That is, 7 is a probable value for K and consequently

$$\sigma_0 = 4 \times 10^4 \text{ e.s.u. approximately.}^1$$

With these values for K and σ_0 it follows that the electrostatic capacity of the Helmholtz double layer condenser would be 20 microfarads, which agrees satisfactorily with the value *ca* 27 microfarads obtained from electrocapillary data for the mercury-water interface. (Of course, this does not imply that the charge density is the same in the two cases.)

The Pressure within the Helmholtz Layer.

We are now in a position to estimate the maximum value of the (mechanical) pressure obtaining within the limiting Helmholtz layer. This quantity p'_{H} is given by :—

$$p'_{\text{H}} = 2\pi\sigma_0{}^2/K$$

With $\sigma_0 = 4 \times 10^4$ and $K = 7$ it follows that $p'_{\text{H}} = 1400$ atmospheres. In the case of the diffuse layer the pressure p'_{ek}, which is given by the expression $p'_{ek} = 2\pi\sigma_{ek}{}^2/K$, is small compared with that in the Helmholtz layer. Thus if we assume a constant value of 80 for the dielectric

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[1] It is noteworthy that this numerical value for σ_0 is practically identical with the result obtained by the method of treatment pursued in the *Trans. Faraday Soc.*, 1932, **28**, 597, to which, however, there are certain objections.

capacity in the diffuse layer and take the case in which a uni-valent electrolyte at concentration 10^{-3} N is present, it follows that δ, the thickness of the diffuse layer, is 10^{-6} cm. Taking ζ to be 40 millivolts it follows that σ_{ek} is approximately 10^3 e.s.u and consequently $p'_{ek} = 7{\cdot}5 \times 10^{-2}$ atmospheres. At greater dilutions p'_{ek} and σ_{ek} would be correspondingly smaller.

When the droplets of an oil-in-water emulsion coalesce to form a coherent layer a certain amount of water, namely that forming the unimolecular layer around each droplet, is released. Prior to release this water has been compressed. Clearly we can neglect the compression effect in the diffuse layer compared with that in the Helmholtz layer. On breaking the emulsion, therefore, an increase in volume due to the destruction of the Helmholtz layer is to be expected. Calculation shows, however, that even with a litre of a 1 per cent. emulsion the increase in volume would only be of the order 10^{-3} c.c.

Energy of Adhesion and Dipole Attractions.

Consider the case of the interface between water and a saturated hydrocarbon oil. From capillary measurements the energy of adhesion is found to be 40-45 ergs per cm.^{2} In view of the very short range forces likely to be involved we may regard this energy as confined practically entirely to the single layer of water molecules adjacent to the oil surface. Since each water molecule has a permanent dipole it is reasonable to suppose that the adhesion has its origin in the creation of an induced dipole in the outer alkyl groups in contact with the water. The alkyl groups themselves have no appreciable permanent moment. On the basis of well-known electrostatic theory the decrease in potential energy or energy evolved in the creation of a dipole under these conditions is given by $\frac{2\alpha\mu^2}{r^6}$ where α is the polarisability of the C—H bond, μ the permanent dipole of water, and r the equilibrium distance between the centre of the water dipole and the centre of the induced dipole. In the light of known atomic and molecular dimensions it will be assumed that r is approximately 2×10^{-8} cm. In view of this magnitude and likewise in view of the fact that the energy term involves a very high power of r it is reasonable to assume that the effective dielectric capacity may be set equal to unity, since it is only the last stage of the process of approach of the water dipole to the hydrocarbon surface which involves any sensible work. Setting $\mu = 1{\cdot}84 \times 10^{-18}$, $\alpha = 0{\cdot}67 \times 10^{-24}$ (for the C—H link) and $r = 2 \times 10^{-8}$ cm., it follows, on this basis of calculation, that the energy set free in the act of adhesion of a single water dipole is $7{\cdot}1 \times 10^{-14}$ ergs, a quantity which is not much greater than the average kinetic energy of translation. At such a surface therefore the energy of attachment, if ascribed to the induction of dipoles, is not great. This would be in agreement with the fact that a hydrocarbon oil surface is hydrophobic as compared with the hydrophilic character of a protein surface where permanent dipoles due to amino, carboxyl, and peptide groupings exist. Regarding the hydrocarbon side of the interface as consisting essentially of methyl groups each of area approximately 20×10^{-16} cm.^{2}, and assuming that the water dipoles are not likely to be aligned more tightly than corresponds to one water dipole per methyl group area, it follows that the number of water dipoles per unit area is 5×10^{14}. On this basis the energy liberated by the act of union would amount to 35 ergs per cm.^{2} (If there be a water dipole per C—H bond the resulting value would be approximately three times this.) This agrees in so far as order of magnitude is concerned with the value (40-45 ergs per cm.^{2}) obtained from capillary measurements; in fact, the degree of agreement is largely fortuitous. It may be concluded, however, that the energy of adhesion could be accounted for on the above basis.

Interfacial Tension in the Absence of Electrical Effects.

On the basis of elementary electrocapillary considerations we can write:—

$$\gamma_0 - \gamma = \text{electrical energy per unit area},$$

where γ is the interfacial tension observed, and γ_0 its value in the absence of electrical effects. If we suppose that sufficient electrolyte has been added to one of the liquids (water) to reduce the thickness of the double layer to its limiting value ($\delta_0 = 3 \times 10^{-8}$ cm.), and at the same time that the electric charge density has reached its upper limit σ_0, we can regard the distribution of electricity at the interface as identical with that of a simple condenser. We then have:—

$$\gamma_0 - \gamma = \frac{2\pi\sigma_0{}^2\delta_0}{K},$$

where K is the dielectric capacity of the space between the plates. For reasons already given we shall take Rideal's estimate of 7 for K in this case.

For the interface, saturated hydrocarbon-water, σ_0 has been estimated to be 4×10^4 e.s.u. For this case therefore it follows that

$$\gamma_0 - \gamma = 43 \text{ ergs per cm.}^2$$

For a saturated liquid hydrocarbon-water interface the observed value of the interfacial energy (γ) is approximately 50 ergs per cm.^{2} It follows therefore that the free interfacial energy hydrocarbon-water would be 93 ergs per cm.^{2} approximately, if the existing electrical effects were removed. The influence of the naturally existing electrical field is therefore very great.[3]

The electrical charge involved is usually ascribed in the case of "pure" water to the preferential primary adsorption of OH$^-$ ions upon the oil surface. The fall in interfacial tension due to this adsorption amounts therefore approximately to 43 dynes per cm. (for the observed interfacial tension in the case of pure water only differs by a dyne or two from that obtained in the presence of a considerable amount of a salt such as KCl). The fact that addition of electrolyte alters the observed interfacial tension to an extent which is almost negligible compared with the effect attributed above to the primary adsorption of the OH$^-$ ions from the water itself, suggests that the charge density attained prior to the addition of any electrolyte is itself very close to the limiting value σ_0. In other words, the charge density may be treated as substantially constant.

It will be recalled that the value ascribed to the upper limit of the charge density per unit area has been obtained on the basis that the electrical energy could be equated in the limit to the work of adhesion of the water molecules at the interface in question. That is :—

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[3] The influence of the electrical field at the liquid-vapour interface has already been considered by Bikerman, *J. Physique*, 1935, **6**, 469.

$$\frac{2\pi\sigma_0^2\delta_0}{K} = \text{work of adhesion} = \gamma_1 + \gamma_2 - \gamma_{12},$$

where γ_1 = free surface energy water-air (73 ergs/cm.^{2}),

γ_2 = ,, ,, ,, organic liquid-air,

γ_{12} = free interfacial energy water-organic liquid.

Also making use of the electrocapillary relation

$$\gamma_{12}^0 - \gamma_{12} = \frac{2\pi\sigma_0^2\delta_0}{K}$$

where γ_{12} is the observed interfacial energy and γ_{12}^0 the value it would have in the absence of electrical effects, it follows that

$$\gamma_{12}^0 = \gamma_1 + \gamma_2$$

By means of this relation, γ^0 terms and ultimately charge density values may be readily obtained. The following table illustrates the magnitude of these terms for a few typical organic substances in contact with water.

Organic Liquid.	Work of Adhesion ergs/cm.	γ_2 ergs/cm.^{2}	γ_{12}^0 ergs/cm.^{2}	γ_{12} ergs/cm.^{2}	σ_0 Charge Density in e.s u.$\times 10^{-4}$.
Paraffins . .	40-45	19-22	92-95	50-52	4
Benzene . .	66	29	102	36	5
Octyl alcohol .	92	27·5	100·5	8·5	5·8
Aniline . .	110	42	115	5	6·4

γ_1 = 73 ergs/cm.^{2}

Let us turn to a very different type of interface, namely that of mercury in contact with water in which the creation of the electric field is not due to adsorption of ions but presumably to surface ionisation. The work of adhesion in this case is 173·8 ergs/cm.^{2} (Harkins) whence the electric charge density is 8×10^4 e.s.u., on the assumption that the magnitude of the adhesional work determines the upper limit of the charge density at the interface in question. The observed interfacial tension γ_{12} being 375 ergs/cm.^{2} [3] the value of γ_{12}^0 is 549 as calculated on the above basis. The value ascribed to γ_{12}^0 is based on Harkins' value for the adhesion mercury/water, which in turn involves the tension mercury-vacuum for which Harkins and Ewing find $\gamma_{\text{Hg-vac.}} = 476$ ergs/cm.^{2} Frumkin [4] has measured the maximum value of the tension at the mercury surface when mercury is in equilibrium with the vapour of a 0·01 normal aqueous electrolyte, the maximum being obtained from electrocapillary data and finds $\gamma_{\text{Hg-vapour over solution}} = 420$ ergs/cm.^{2} (in round numbers). Employing this value to calculate the adhesion between mercury and the aqueous solution one obtains work of adhesion = 118 ergs/cm.^{2} a quantity appreciably lower than that based on the $\gamma_{\text{mercury vacuum}}$ datum. The electric charge density now becomes $6{\cdot}6 \times 10^4$ e.s.u. and $\gamma_{12}^0 = 493$ ergs/cm.^{2} Frumkin [5] has found by direct experiment that at the interface : mercury-1-normal NaCl saturated with Hg_2Cl_2 the charge density is 15 × 10^4 e.s.u. ; at the interface : mercury-1-normal KOH saturated with HgO, 6 × 10^4; and at the interface: mercury-2-normal H_2SO_4 saturated with Hg_2SO_4, 11·7 × 10^4 e.s.u. These results are, of course, quite independent of the assumption that there is a possible connection between adhesional work and charge density. On the latter basis the values for the charge density have been calculated to lie between 6·6 and 8 (× 10^4) e.s.u. It would appear therefore that the adhesional work hypothesis is roughly correct. Unfortunately no similar check based on electrocapillary measurements is possible for the interface between an organic liquid and water.

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[3] Bartell, Case and Brown (*J. Amer. Chem. Soc.*, 1933, **55**, 2419), find (at 25° C.) $\gamma_{12} = 374{\cdot}1$ dynes/cm., by the drop weight method, and $\gamma_{12} = 375$ dynes/cm. by the capillary rise method.

[4] Frumkin, *Physikal. Zs. Sowjetunion*, 1932, **1**, 255.

[5] Frumkin, *Z. physikal. Chem.*, 1923, **103**, 55.

Summary.

On the assumption that the energy of adhesion at an interface is a measure of the upper limit which can be ascribed to the energy of the condenser due to the Helmholtz double layer of electricity associated with the interface, values may be obtained for the (maximum) charge density at the interface water-organic liquid in a number of cases. It is shown that the value so obtained leads to a reasonable value for the electrostatic capacity of the double layer and further, in the only case in which direct experimental test is available, namely the interface mercury-aqueous solution of electrolyte, the charge density calculated on the above basis agrees as to order of magnitude with that obtained from electrocapillary data.

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THE VISCOSITIES OF LIQUID MIXTURES WITH PYRROLE AS A COMPONENT.

By Mladen Dezelic.

In continuance of a former investigation,[1] we have studied the viscosities of liquid mixtures in which pyrrole constitutes one component in order to determine the readiness of unsubstituted pyrroles to form addition compounds.

It has already been shown [2] that di- and poly-nuclear pyrrole derivatives exhibit an increased tendency to form complexes. The capacity of mono-nuclear pyrroles to form complexes depends upon the substituents and increases with their number. Owing to the weak basicity of its nitrogen, pyrrole itself has only a slight tendency to form addition compounds with organic acids and substances of an acid character. With picric acid,[3] triphenylmethane,[4] and trinitrobenzene [5] it forms unstable molecular compounds. Its imide hydrogen cannot be replaced by the nitro-group, although an alkyl- or acetyl-group can be substituted. On the other hand, it is well known that in the presence of metallic potassium or upon boiling with potassium hydroxide, the

[1] M. Dezelic, *Annalen*, 1935, **500**, 290.

[2] Comp. H. Fischer and H Orth, *Die Chemie des Pyrrols*, 1934, Vol. I, p 316.

[3] S. C. Hooker, *Chem. Zentralblatt*, 1891, **1**, 354 ; A. Treibs and P. Dieter, *Annalen*, 1934, **513**, 78.

[4] H. Hartley and N. G. Thomas, *J. Chem. Soc.*, 1906, **89**, 1013.

[5] P. van Romburgh, *Rec.*, 1898, **14**, 68.

potassium salt of pyrrole will be formed. Unsubstituted pyrrole and the lower alkyl pyrroles are easily polymerised by suitable catalysts, particularly in the presence of mineral acids. The polymerised pyrroles show properties quite different from those of the initial compounds; with the exception of N-substituted pyrroles, they are able to form molecular compounds.[2]

It was our aim therefore to procure additional knowledge about the properties of unsubstituted pyrrole and to ascertain whether it will form complexes with basic or with acid substances. In our investigations on the formation of molecular compounds of pyrroles,[1] we used thermal analysis; this method, however, could only be employed in the case of pyrroles which crystallise readily. Unsubstituted pyrrole, being a liquid which will not crystallise, we determined the internal friction with a view to drawing conclusions from the change in the viscosity of the binary systems, as to whether formation of complexes had taken place. The present investigation deals with ten binary systems, with pyrrole as one component, and pyridine, piperidine, quinoline, nicotine, diethylamine, chloroform, acetic acid, *n*-butyric acid, allyl-iso-thiocyanate and nitrobenzene respectively, as the other. It was found that all of these substances which are basic form complexes with pyrrole, while the others are indifferent to pyrrole.

Significance of the Viscosity-concentration Curves.

From the nature of the viscosity curves we can, under certain conditions, form conclusions as to the formation of complexes or compounds. If the curve of viscosity η against the proportion of mixture c, shows a maximum or a convexity with respect to the axis of concentration, it is usually assumed that the components form new complexes or compounds in the liquid phase. In this connection Dunstan and Thole[6] found that, in general, associated liquids possess relatively high viscosities and they concluded from this, that a maximum in the viscosity curve indicates even closer association or complex-formation. It follows that falling curves and minima are to be attributed to dissociation.

It has still to be decided, however, whether it may be assumed that, in every case, maxima in the viscosity curve indicate the formation of compounds or complexes. It is therefore always advisable also to determine the melting-point or vapour-pressure curves. A. Bramley[7] showed that viscosity cannot of itself be used as a proof of the existence and composition of a compound in a liquid mixture. Only in a few special instances can any conclusion be drawn from the position of the maxima in the viscosity curve, as to the proportionality of the two components in the new compound. The maximum shifts towards the side of the more viscous component under the influence of temperature and dissociation. It is possible that the maximum of internal friction or viscosity may coincide in position with the composition of the compound, as in the case of pyrrol-piperidine. This will probably occur when the compound is present in the mixture in such a considerable concentration that, as a result of the increase in size of the molecules, the liquid shows a markedly increased viscosity.[8]

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[6] Dunstan and Thole, *The viscosity of liquids*, 1917, p. 44.

[7] A. Bramley, *J. Chem. Soc.*, 1916, **109**, 10, 434, 469.

[8] Comp. R. Kremann, *Die Eigenschaften der binären Flüssigkeitsgemische*, 1916; E. Hatschek, *Die Viskosität der Flüssigkeiten*, 1929. The English original published 1928.

If, however, heat is generated upon admixture of the components, and, at the same time, a maximum or convexity with respect to the axis of concentration is observed (as occurred during this investigation in the systems containing pyrrole and strong organic bases), there can be no doubt as to the formation of such complexes or compounds.

Experimental.

The liquids used were " puriss " or " suitable for scientific purposes " (Merck and Schering-Kahlbaum), and were twice distilled. Two pyrroles of different origin (E. Merck and I. G. Farbenindustrie A.G. respectively), were used. The Merck pyrrole was first dried and twice distilled, the fraction between 129°-131° C. being employed for the viscosity measurements. The I.G. pyrrole was purified in the same way, with the additional precaution that its potassium salt was prepared first.

All viscosity measurements were carried out in the Ostwald viscometer, modified according to Jones and Veazey.[9] The size of the capillaries and the viscometer were so chosen, that the transpiration time for water at 20° C. was approximately 100 secs. For the measurement of the specific gravity the Ostwald pyknometer was used, capillary constrictions having been made onboth arms to avoid loss by dripping and evaporation.

Measurements were carried out both at 15° C. and 20° C., the temperature being kept constant to within ± 0·1°. The volume of liquid used for the viscosity measurements was always the same at constant temperature, *viz.* approximately 6 c.c., the volume of the pyknometer.

The viscosity was calculated from the formulae :—

$$\eta_{15} = 0{\cdot}01138\frac{dt}{t_0} \quad \text{or} \quad \eta_{20} = 0{\cdot}01005\frac{dt}{t_0}$$

where d is the specific gravity of the liquid at 15° C. or 20° C. as compared with water of the same temperature, t the transpiration time of the liquid and t_0 the transpiration time of water at the same temperature, 0·01138 and 0·01005 being the viscosities of water at 15° C. and 20° C. respectively, in absolute units poises.[10] All the values for viscosity we give are expressed in terms of poises.

In order to save space, the results of the measurements are reproduced in the form of curves, but one table, that of pyrrole-piperidine, is given as an example of the measurements on which the curves are based. In every case the specific gravity curve (density D_4^t) is given in addition to the viscosity curve.

TABLE I.—PYRROLE-PIPERIDINE (20° C.) (FIG. 1).

Mol. Per Cent. Piperidine.		$\eta_{20} \times 10^4$.	
0	0·9531	131·5	75·3
20	0·9318	162·9	61·4
30	0·9217	181·1	55·2
40	0·9172	200·0	50·0
50	0·9050	207·1	48·3
60	0·9000	202·7	49·3
70	0·8918	195·6	51·1
80	0·8847	181·6	55·0
90	0·8772	173·9	57·5
100	0·8630	166·4	60·1

The viscosity of pyrrole was measured several times at 15° and 20° C. The two preparations used showed no appreciable difference with respect to their viscosity and density. The average values are :—

Pyrrole : $D_4^{15} = 0{\cdot}9578$ $\eta_{15} = 0{\cdot}01423$
,, $D_4^{20} = 0{\cdot}9531$ $\eta_{20} = 0{\cdot}01315$

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[9] H. C. Jones and W. R. Veazey, *Z. physik. Chem.*, 1905, 61, 641.

[10] Thorpe and Rodger, *Phil. Trans.*, 1894, 185, 449; calculated by Stöckl (Landolt-Börnstein, *Phyik.-chem. Tabelieu*, 5. Aufl. 1923, p. 136).

Pyrrole-Piperidine (20° C.) (Fig. 1).*—The η-curve of this system has the most clearly defined maximum, corresponding to a 50 mol.-per cent. concentration of each component. The considerable increase in viscosity is probably due to the presence of the newly formed compound in the liquid mixture. During the mixing of the components the temperature rises, especially when the components are mixed in a proportion of 50 mol.-per cent. respectively. The course taken by the specific gravity curve is almost that of a straight line.

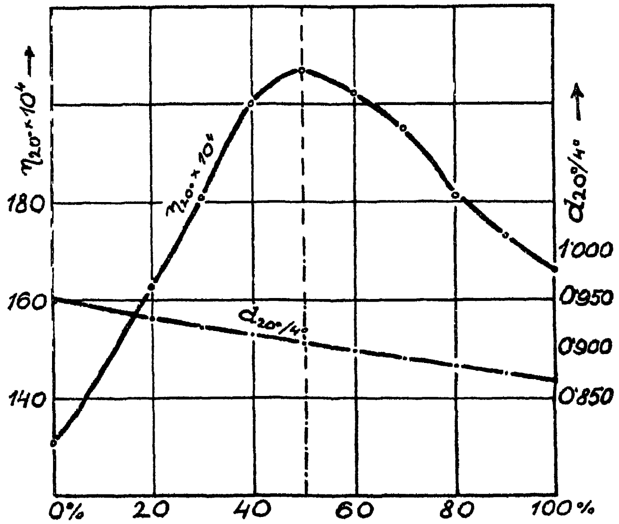

FIG 1.—Pyrrole and Piperidine. Absc. · Mol.-per cent. Piperidine.

Pyrrole-Pyridine (15° C.) (Fig. 2).—Here the maximum in the viscosity curve occurs between the concentrations of 20-30 mol.-per cent. pyridine, thus showing a marked displacement towards the more viscous component. The specific gravity curve is slightly convex with respect to the axis of concentration.

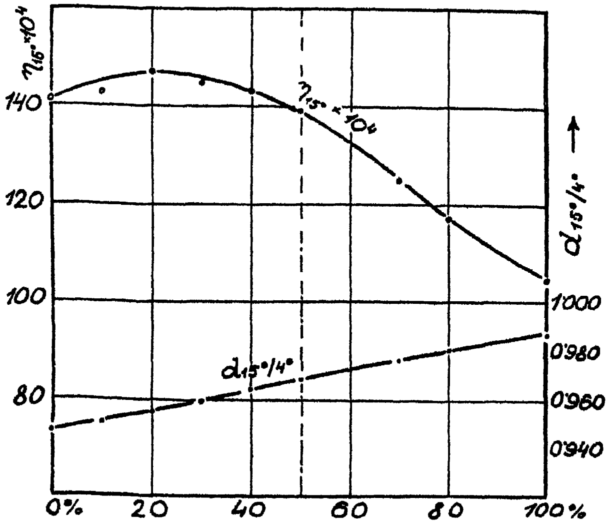

FIG. 2.—Pyrrole and Pyridine. Absc.: Mol.-per cent. Pyridine.

Pyrrole-Nicotine (20° C.) (Fig. 3).—The viscosity curve shows a definite maximum at a concentration of approximately 60 mol.-per cent. nicotine. The specific gravity curve is also definitely convex with respect to the axis of concentration, which shows that a contraction of the mixture has taken place. During the mixing-process the temperature of the liquid rises.

* D_4^{20} = density, η = viscosity and ϕ = fluidity.

Pyrrole-Quinoline (20° C.) (Fig. 4).—The viscosity curve is definitely convex with respect to the axis of concentration. The specific gravity curve likewise shows a slight convexity. Upon mixing the components a rise in the temperature of the mixture occurs.

Pyrrole-Diethylamine (15° C.) (Fig. 5).—At first the viscosity curve is definitely convex with respect to the axis of concentration, up to a concentration of 60 mol.-per cent. diethylamine; at higher concentrations, however, it becomes concave. The mixing of the components is accompanied by a rather marked evolution of heat, so that cooling of the mixture was found necessary because of the volatility of the diethylamine. These facts point to the formation of new complexes. The course taken by the specific gravity curve is almost a straight line.

Pyrrole with Organic Acids, etc.—The internal friction and specific gravity of the binary systems of pyrrole with, respectively, glacial acetic acid, *n*-butyric acid, chloroform, allyl *iso*thiocyanate and nitrobenzene were also investigated. In none of these systems was any maximum or convexity of the curves observed; on the contrary they were invariably concave. No evolution of heat could be observed upon mixing the components.

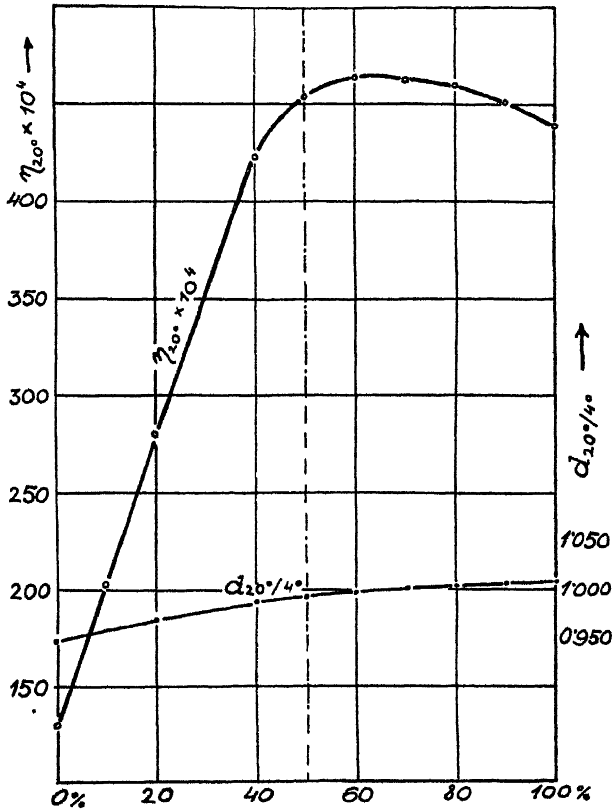

FIG. 3.—Pyrrole and Nicotine. Absc.: Mol.-per cent. Nicotine.

Discussion.

The ten binary systems investigated can be divided, according to the type of η curve, into three groups: (1) Those in which the viscosity curve shows a maximum (pyrrole-pyridine, pyrrole-nicotine and pyrrole-piperidine). (2) Those in which the viscosity curve is convex with respect to the axis of concentration but shows no maximum (pyrrole-quinoline and pyrrole-diethylamine). (3) In which the viscosity curve takes a course which is more or less concave (pyrrole with chloroform,

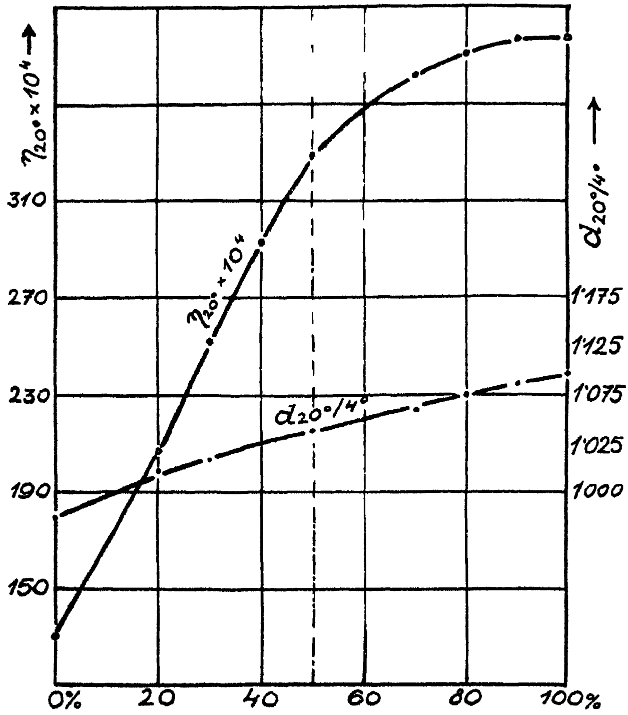

Fig. 4.—Pyrrole and Quinoline. Absc.: Mol.-per cent. Quinoline.

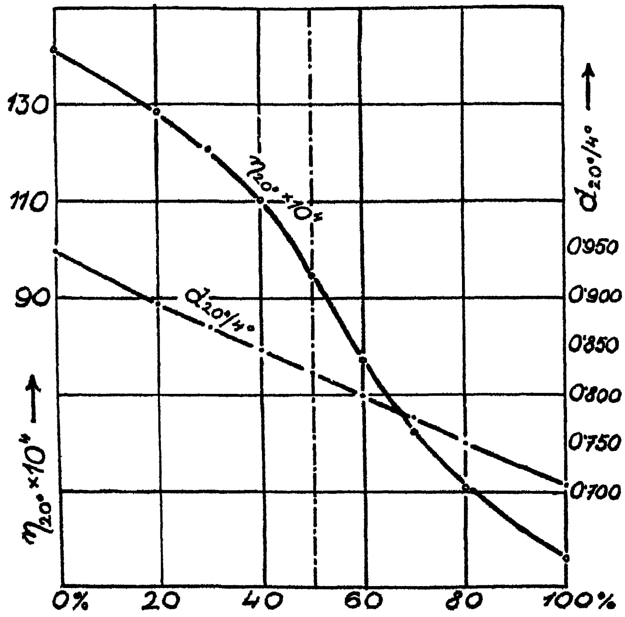

Fig. 5.—Pyrrole and Diethylamine. Absc.: Mol.-per cent. Diethylamine.

glacial acetic acid, *n*-butyric acid, allyl-*iso*-thiocyanate or nitrobenzene).

From the fact that in groups 1 and 2 heat was evolved on mixing as well as from the course taken by the viscosity curves, it may be assumed that the components of these systems have formed complexes or molecular compounds, but in group 3 no evolution of heat being observed, we have no proof that compounds are formed by the components in the liquid phase, since, as has already been observed, it is not possible to determine the composition of compounds from their viscosity curves alone.

In the single case of pyrrole-piperidine, where a marked maximum occurs at a concentration of 50 mol.-per cent., we can say that the components have entered into equi-molecular composition. In the systems containing pyridine and nicotine respectively the maxima shift markedly towards the side of the more viscous component, but as has already been stressed, this may be explained by dissociation of the complexes formed.

Our investigations show that unsubstituted pyrrole will form complexes, or molecular compounds, with organic substances of a basic character, while it is indifferent to weak organic acids and substances of an acid character. From these facts we conclude that the acid properties of pyrrole are more pronounced than the basic ones. It may be assumed that it is the hydrogen of the imino-group in the pyrrole ring which gives it these acidic properties.

Investigations of the Raman spectra of pyrrole provide indications in favour of the above conclusions. These Raman spectra indicate that pyrrole has either an olefinic or an aromatic configuration, according to the distribution of its electrons.[11] The basic or acidic properties of the pyrroles, are determined by these configurations. Unsubstituted pyrrole with well-defined aromatic C—H lines in the Raman spectrum, as well as most of the mono-alkyl pyrroles, belong to the so-called "acid" pyrroles. The C-polyalkyl pyrroles on the other hand, the so-called "basic" pyrroles, exhibit a strengthening of the olefinic properties.[12]

Summary.

The viscosity and specific gravity of binary systems containing pyrrole with piperidine, pyridine, nicotine, quinoline, diethylamine, chloroform, glacial acetic acid, *n*-butyric acid, allyl *iso*thiocyanate and nitrobenzene, respectively, were investigated.

The first five substances, of a basic character, formed complexes or molecular compounds with pyrrole. The viscosity curve of the first three of these systems was characterised by a maximum and that of the following two by a convexity. All five showed a rise in temperature during the mixing of the components.

The last five systems have concave viscosity curves, and do not evolve heat on admixture of the components. In these systems the components apparently form no complexes or compounds in the liquid phase.

These results afford proof of the fact that the acid characteristics of unsubstituted pyrrole are much stronger than the basic ones. This accords with the results of the investigation of the Raman-spectra of pyrrole, according to which pyrrole would have "acid" properties, as compared with substituted pyrroles.

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The University of Zagreb,
Jugoslavia.

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[11] S. Venkateswaran, *Indian J. Physics*, 1930, **5**, 145; G. B Bonino, R. Manzoni-Ansidei and P. Pratesi, *Z. physik. Chem B*, 1933, **22**, 21; 1934, **25**, 348; A. Stern and K. Thalmayer, *Ibid.*, 1936, **31**, 403.

[12] P. Pratesi, *Gazz. chim. ital.*, 1935, **65**, 658.

REVIEWS OF BOOKS.

The Hardness of Metals and Its Measurement. By HUGH O'NEILL, D.Sc., M.Met. 1935. (Chapman & Hall. Ltd, London. Pp. xiv and 292. 25s. net.)

Hardness, although undoubtedly a characteristic property of metals and of the utmost importance from the point of view of their practical use, is probably one of the most difficult to measure accurately. So at least would appear to be the opinion of Dr. O'Neill, who likens the hardness of metals to the storminess of seas, both being easily appreciated but not readily measured. And if one takes account of all the methods which have been proposed to gauge this important property and, still more, if one studies in Dr. O'Neill's book, the variations in the results obtained by the use of these various methods, one must conclude that it is far from easy to obtain a true measure of metallic hardness.

A first difficulty is the selection of a suitable criterion and even now, after many years of experiment and testing, opinion is not unanimous. Most frequently, however, modern practice takes resistance to penetration as the specific factor on which measurements are to be based. In so doing, it follows the opinion of St. Thomas Aquinas, who wrote in A.D. 1260, " the hard is that which resists pressure or division." Aquinas' modern discipline, however, soon finds that thirteenth century wisdom, though doubtless profound in its way, is by no means a complete answer to present day troubles. Metals resist penetration at first elastically, but afterwards, as the load increases, in a plastic manner. Are both of these to be taken as the basis of measurement, or only one ? In the latter case, which is to be preferred ? Nowadays, measurements are generally based on the plastic effect, i.e. the permanent deformation left after the indenting load has been removed, but opinion in the past has not been unanimous on this choice. For example, Hertz in 1896 considered that the hardness of a body should be measured by the maximum pressure it would resist, under stated conditions, consistent with perfect elasticity. Even if agreement is reached on this point, however, a complete solution to the problem is still lacking. The plastic indentation of a metal by some form of indenting tool—be it a sphere, cone or other shape—brings into play two separate properties of the indented metal, namely, its initial hardness and the rate at which this hardness increases as a result of deformation. The relative importance of these two properties is likely to vary with degree of deformation, and as metals having approximately the same initial hardness may vary quite considerably in their rate of hardening when deformed, it may be expected that the hardness values they give under specific testing conditions will not be independent of the degree of deformation thereby produced. It is not surprising, therefore, that in most practical hardness testing methods, the conditions of testing are carefully standardised.

There are, of course, other methods of testing which involve different criteria—for example, the method of rebound utilised in the Shore Scleroscope—and most of these are also subject to variables.

A discussion of all these methods, their susceptibility to variations in testing conditions, the specific properties on which they depend, their correlation one with another, may be expected to be complex, but it has been tackled in a very thorough manner by Dr. O'Neill. He deals with the underlying principles of each method of testing, with the machines used for the test and with the effects of all sorts of variables in testing conditions. Possibly his book may not appeal so much to those who are merely concerned with the everyday testing of hardness in a more or less routine manner, but, to the student who is interested in knowing the actual properties he is measuring, the limitations of the methods he is using, and particularly if he wishes to correlate hardness measurements with other useful properties of metals, Dr. O'Neill's analysis of the subject is invaluable.

The Casting of Brass Ingots. By R. GENDERS and G. L. BAILEY. (The British Non-Ferrous Metals Research Association, London, 1935. Pp. xv and 191. 15s. net.)

The casting of an ingot is an extremely important stage in the manufacture of almost all wrought metal products because, in most cases, if the ingot is defective, the defects present are either retained in greater or less degree in the finished article, or they are eliminated only with difficulty and expense. Hence, it is of prime importance to obtain a sound ingot, a fact which was realised years ago in the iron and steel industry, with the result that the problem of securing such an ingot has been the subject of much investigation by the research laboratories and steelmaking departments of many firms in that industry and has led, in recent years, to a very comprehensive study of the whole matter by a special committee of the Iron and Steel Institute and the British Iron and Steel Federation. This study has shown that certain types of defects may be prevented, whereas others are more or less unavoidable, though their position and extent may be controlled.

Very probably, there has not been the same incentive in the non-ferrous industry to study ingot making conditions with the same intensity, possibly because the products of that industry have not been subjected, as a rule, to such rigorous inspection as have wrought steel products. However, the results of ingot defects have been sufficiently marked in the case of one particular product—brass strip—to lead to an exhaustive examination of ingot production by the Non-Ferrous Metals Research Association who have published an account of their investigations in a Monograph having the title given above. In essentials, the problems are similar to those in the casting of steel ingots, but there are differences. For example, the type of ingot used, being very thin, leads to very rapid solidification, much more rapid than occurs in most steel ingots, with the result that the progress of solidification is not quite the same as in the thicker steel product. Again, the type of oxide skin formed on the non-ferrous metal exercises a very considerable effect on the production of surface defects, and this leads to several peculiar problems in the production of brass ingots.

The subject has been well handled by the two authors, who have carried out the greater part of the very extensive investigations on which the results given in the book are founded. They have isolated and separately tested many variables, and have drawn informative conclusions from the results of these specially controlled experiments. There is no doubt that the volume will be of considerable use to the brass industry in improving ingot quality and hence that of the rolled strip. The book, in fact, provides a good example of the value of co-operative research in tackling a problem which might well be regarded as beyond the resources of individual firms. Although dealing essentially with a particular product of the non-ferrous industry, the book contains much which is of interest and value to those concerned with the production of sound ingots of other metals, as well as to metallurgists generally.

Practical Photomicrography. J. E. BARNARD and F. V. WELCH. Third Edition, 1936. (Edward Arnold & Co., London. Pp. xii and 352. 21s. net.)

"Barnard and Welch" is well known as one of the best books in the English language on the art and science of photomicrography. In preparing the new edition, the authors have revised the text (the previous edition appeared eleven years ago) and, besides enlarging several sections—particularly that dealing with the photomicrography of metals—have added a new chapter on the use of ultraviolet light. Like its predecessors, the new edition will be welcomed as giving a sound practical and scientific treatment of a most interesting and important subject.

Metallurgy: An Elementary Treatise. By E. L. RHEAD, M.Sc., F.I.C. New and Revised Edition, 1935. (Longmans, Green & Co., Ltd. Pp. iv and 382. 10s. 6d. net.)

A metallurgical book which has run to six editions, in addition to a number of "new impressions," has obviously served a very useful purpose. Doubtless, many students of metallurgy and engineering, particularly those connected with the Manchester College of Technology, where the author of this book was lecturer for many years, have perused its pages in search of metallurgical knowledge.

The new edition follows on similar lines to those immediately preceding it in giving a brief outline—necessarily very condensed—of metallurgical processes. Much of the text has been rewritten in order that reference could be made to modern developments.

ERRATA.

On pages 592 and 594 the numbered figures are wrongly inserted: Fig. 1 should be numbered Fig. 3 and *vice versa.*

ABERDEEN: THE UNIVERSITY PRESS

THE CENTRIFUGE METHOD OF INVESTIGATING THE VARIATION OF HYDROSTATIC PRESSURE WITH WATER CONTENT IN POROUS MATERIALS.

By R. J. Schaffer, J. Wallace and F. Garwood.

Received 8th February, 1937.

The hydrostatic pressure to which water held in the pores of a porous material is subjected varies with the curvature of the liquid film. It is related to the moisture content in a manner that depends on the structure of the particular material under consideration, and this relation has been used to characterise the capillary properties of a porous material such as stone, brick or soil. There are various methods of studying this relation. Wilsdon [1] has recently discussed the subject and Wilsdon, Bonnell and Nottage [2] have studied the hydrostatic, osmotic and vapour pressure methods.

Another method, which involves the use of the centrifuge, has been applied in investigating the moisture relations of soils. Briggs and McLane [3] measured the " moisture equivalent " of a soil, which they defined as " the percentage of water retained by a soil, when the moisture content is reduced by means of a constant centrifugal force until it is brought into a state of capillary equilibrium with the applied force."

The work of Thomas,[4] confirmed by Joseph and Martin,[5] showed that the moisture equivalent of a soil decreased as the weight and thickness of the sample were increased. Veihmeyer, Israelson and Conrad [6] observed a moisture gradient in a centrifuged soil, the moisture content increasing with increasing distance from the axis of rotation.

The present paper deals with investigations on the centrifuge method and with a comparison of the results obtained by the hydrostatic and centrifuge methods using Portland stone as the porous material. The use of a rigid body like Portland stone has advantages over that of a plastic soil, since there is no risk of differential compacting of the material in the centrifuge.

Experimental.

The centrifuge was specially designed. The carrier head consisted of three circular, nickel-steel plates, 17·8 cm. in diameter, the middle plate being 3·3 cm. in thickness. There were six symmetrically disposed cavities in the middle plate equidistant from the axis of rotation, 3·7 × 3·3 × 3·2 cm. in size. Except for small holes leading to the periphery of the plate, to allow for drainage of water, the cavities were totally enclosed by the other two plates, 0·5 cm. in thickness, as shown in Fig. 1. The machine was mounted in a room kept at a constant temperature of 20° C., and was belt driven by a D.C. motor.

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[1] B. H. Wilsdon, *J.S.C.I.*, 1934, **53**, 397T.

[2] B. H. Wilsdon, D. R. G. Bonnell and Miss M. E. Nottage, *Trans. Faraday Soc.*, 1935, **31**, 1304 ; 1936, **32**, 570.

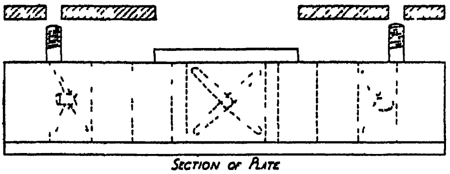
[3] L. J. Briggs and J. W. McLane, *U.S. Dept. of Agric. Bureau of Soils, Bull.* No. 45, 1907.

[4] M. D. Thomas, *Soil Sc.*, 1921, **11**, 409.

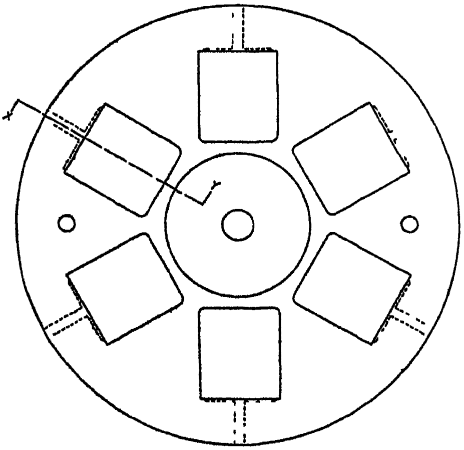
[5] A. F. Joseph and F. J. Martin, *J. Agr. Sc.*, 1923, **13**, 49.

[6] F. J. Veihmeyer, O. W. Israelson and J. P. Conrad, *Agric. Exptal. Stn., Berkeley, California. Tech. Paper*, No. 16, 1924.

With only a pad of filter paper and a thin, perforated duralumin sheet on the outside of each cavity, evaporation of water from specimens was found to be a serious source of error. By inserting a rubber pad between the filter paper and the outside of each cavity, and by placing the specimens in thin copper boxes, open at the outer face, the loss of water by evaporation was greatly diminished.



SECTION OF PLATE



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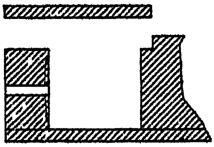

SECTION X-Y

FIG 1 THE CARRIER HEAD

A Haslar tachometer was used to measure the speed of revolution of the centrifuge. At 2050 rev. per min. the speed remained constant to within ± 25 rev. per min.

Three different samples of Portland stone, A, B and C, were used. The total volume of the pores was determined by saturation in vacuo. The maximum error in this determination was less than 1 per cent. The average porosities were 17·5, 20·8 and 18·7 per cent. by volume respectively.

Preliminary experiments showed that equilibrium was attained after three to four hours' centrifuging. In the following experiments the stones were saturated with water in vacuo, and were centrifuged for four hours. The equilibrium water contents of the specimens are expressed in the Tables as percentages of the total saturation values.

Variation of Equilibrium Water Content with Size of Specimen.—To investigate the variation of equilibrium water content with size of specimen, five rectangular specimens of the same cross-section (about 3 × 3 cm.) but of different lengths, *viz.*, 0·5, 1·0, 1·5, 2·0, 2·5 cm., were prepared from a block of Portland stone, B. Each of these was saturated and centrifuged to equilibrium at a constant speed, the outer face of each specimen being at the same distance from the centre of the centrifuge. It was found that as the radial length of the specimen increased the water content decreased. A typical result, at a speed of 1850 rev. per min., gave water contents for these specimens of 74·0, 70·6, 69·0, 67·0 and 66·5 respectively, and is of the same character as that recorded by Thomas.[4]

Distribution of Water along the Radial Length of a Centrifuged Specimen.—Five rectangular blocks of stone A, of dimensions 0·5 × 2·9 × 2·9 cm., were prepared with ground faces to form a composite block 2·5 × 2·9 × 2·9 cm. in size, which was saturated and centrifuged to equilibrium at a speed of 3000 rev. per min.

As is shown in Fig. 2, the water content of each piece increased as its distance from the axis of the centrifuge increased. The moisture gradient is even more pronounced than that found by Veihmeyer, Israelson and Conrad.*

The distribution experiment was repeated with thin metal grids dividing the composite block in various ways. A typical result with a grid dividing the block into two parts (1′, 2′, 3′ and 4′, 5′) is also shown in Fig. 2. It will be seen that the introduction of a grid produces a discontinuity in the curve, and that there is a non-uniform distribution of water along the radial lengths of the two parts.

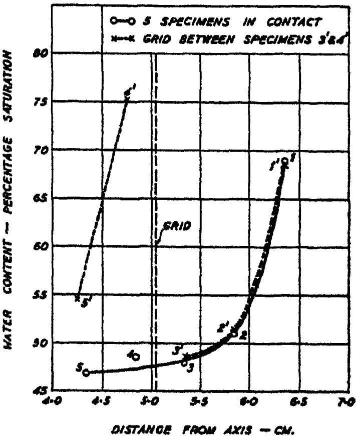

FIG 2 VARIATION OF WATER CONTENT WITH DISTANCE FROM AXIS OF CENTRIFUGE WITH AND WITHOUT THE PRESENCE OF A GRID

Effect of Speed on the Radial Distribution of Water.—The effect of speed on the radial distribution of water was next investigated. Composite specimens of stones A, B and C similar to that described above were used, and, in order to eliminate chance variation due to variability in structure of the material, five runs were made with different arrangements so that each specimen occupied each of the five positions in turn. Experiments were made at speeds of 820, 1050, 1300, 1670 and 2050 rev. per min. The mean water content for each position, expressed as a percentage of the total saturation value, is given in the last three columns of Table I., and the radial distance to midpoint of each specimen in column 1. The values of $\bar{H}(\omega, r)$ in column 3 will be referred to later.

Effect of Variation in the Outer Radius on the Radial Distribution of Water.—To determine the effect on the water distribution of varying the distance of the outer face of the centrifuged sample from the axis of rotation, the same specimens and a similar technique were used. Three series of experiments were carried out at 1300 rev. per min. Composite blocks of four, three and two specimens respectively were so arranged that the distance of the outer face from the axis ($= b$) had three different values, *viz.*, 5·83, 5·33 and 4·83 cm. The results are shown in Table II. Those for five specimens ($b = 6·61$ cm.) centrifuged at this speed are to be found in Table I.

Discussion.

In all the distribution experiments the water content in any one centrifuged specimen increases with increasing distance from the axis of rotation. This is at first sight unexpected because the centrifugal acceleration increases as the radius increases. But, by considering the relationship between the water content and the hydrostatic pressure in

---

* Ref. 6, pp. 24, 29.

TABLE I.—EFFECT OF SPEED ON THE RADIAL DISTRIBUTION OF WATER.

Radial Distance to Mid-point of Specimen. (cm.).	Speed in rev./min.	$\bar{H}(\omega, r)$.	Mean Water Content Per Cent. Total Saturation.		
			Stones.		
			A.	B.	C.
6·36	820	155	98·2	97·7	89·9
5·86		132	97·5	95·5	67·0
5·36		111	96·4	91·7	53·0
4·86		91	95·3	86·4	47·5
4·36		74	92·9	80·8	44·6
6·36	1050	254	96·8	95·2	68·8
5·86		216	95·7	89·3	50·1
5·36		181	92·5	80·1	42·6
4·86		150	85·7	74·0	40·0
4·36		122	78·8	69·7	38·5
6·36	1300	389	96·3	89·7	53·0
5·86		331	93·4	74·8	41·6
5·36		278	84·3	68·1	38·5
4·86		230	75·0	65·6	37·0
4·36		186	68·7	63·8	36·2
6·36	1670	642	92·1	84·2	50·8
5·86		546	74·8	67·9	38·6
5·36		459	63·2	62·4	36·3
4·86		379	59·0	61·0	35·2
4·36		307	56·5	60·2	34·4
6·36	2050	967	86·8	74·5	43·6
5·86		823	63·9	61·2	36·0
5·36		692	55·8	58·8	34·4
4·86		572	53·4	57·9	33·7
4·36		463	52·1	57·3	33·0

TABLE II.—EFFECT OF VARYING OUTER RADIUS ON THE RADIAL DISTRIBUTION OF WATER. SPEED OF CENTRIFUGE 1300 REV. PER MIN.

No. of Specimens.	Distance of Outer Face from Axis of Centrifuge cm. (= b).	$\bar{H}(\omega, r)$.	Water Content Per Cent. Total Saturation.		
			Stones.		
			A.	B.	C.
4	5·83	301	96·2	94·6	76·2
		251	95·3	84·0	50·0
		205	92·4	73·9	41·2
		164	81·5	67·0	37·8
3	5·33	251	96·3	94·4	79·6
		205	95·9	87·7	49·7
		164	91·8	72·1	42·0
2	4·83	205	96·7	94·7	82·3
		164	96·1	89·9	53·4

the centrifuged specimen, following the lines set out in the following paragraphs, this apparent anomaly can be explained, and all the experimental results can be correlated one with another.

Whatever be the structure of the porous material it will be assumed that the pores are all inter-connected and that, if water saturates the material and is later partly driven out by centrifuging, there is still hydrostatic connection throughout. That is, the hydrostatic pressure is assumed to be continuous throughout the specimen.*

Equation for Pressure Deficiency.

Consider a small element of volume situated entirely in the water phase at a distance r from the axis of the centrifuge. The forces on the water inside the element consist of its weight and the hydrostatic pressure P of the surrounding water, acting everywhere normal to the surface of the element. The acceleration $\omega^2 r$ of the element is large compared with that of gravity, and therefore the effect of the weight will be neglected. Since the acceleration is everywhere radial and is proportional to the radius it follows that P is constant at all points equidistant from the axis, and

$$\frac{\partial P}{\partial r} = \rho\omega^2 r \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Since the pressure deficiency p is equal to $P_0 - P$,

$$\frac{\partial p}{\partial r} = -\rho\omega^2 r \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Integrating with respect to r

$$p = C(\omega) - \rho\frac{\omega^2 r^2}{2} \quad . \quad . \quad . \quad . \quad (3)$$

where $C(\omega)$ is independent of r but may depend on ω.

It is convenient to express the pressure deficiency by the equivalent height of water :—

$$h = \frac{p}{g\rho} = A(\omega) - H(\omega, r) \quad . \quad . \quad . \quad (4)$$

where $$A(\omega) = \frac{C(\omega)}{g\rho}$$

and $$H(\omega, r) = \frac{\omega^2 r^2}{2g} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

---

* The following notation will be used throughout :—

P_0 = atmospheric pressure (dynes/cm.^{2}).
P = hydrostatic pressure (dynes/cm.^{2}).
$p = P_0 - P$ = pressure deficiency (dynes/cm.^{2}).
$h = \frac{p}{g\rho}$ = pressure deficiency expressed as height of column of water (cm.).
ρ = density of water (gm./c.c.).
n = speed of centrifuge (rev./min.).
ω = angular velocity of centrifuge (radians/sec.).
r = radial distance to any point (cm.).
b = distance of mid-point of outer face of composite block of specimens from axis of centrifuge (cm.).
a = radial distance of edges of composite block of specimens, parallel to and furthest from axis of centrifuge (cm.).
W = equilibrium water content at any point (per cent. total saturation).
γ = curvature of water-air film (cm.$^{-1}$).
σ = surface tension of water-air film (dynes/cm.).
ψ = capillary potential (ergs/gm.).

In writing the arbitrary constant of integration as a function of ω it is assumed that all other conditions are kept constant.

The Relation between Water Content and Pressure Deficiency.

In the case of a hypothetical porous material made up of packed spheres the water at low percentage saturations can be assumed to occupy rings around the points of contact of adjacent spheres. From geometrical considerations it is obvious that, as the water content W increases, the curvature γ of the water-air surface decreases and *vice versa*. This is assumed to hold for any porous material and for all values of W. If there is complete wetting, and therefore zero angle of contact, the relation between W and γ for any porous material may be written as a single-valued, continuous function

$$W = \mathrm{f}(\gamma)\,;$$

since $p = \gamma\sigma$ this becomes

$$W = \mathrm{f}\left(\frac{p}{\sigma}\right) = F(p) \qquad . \quad . \quad . \quad . \quad (6)$$

where W decreases as p increases.

From equation (3) it is obvious that as r increases p decreases. W therefore increases. That is, the water content increases towards the outside of the specimen. This deduction agrees with the results shown in Fig. 2.

Assuming now that the variation of water content with distance from the outer face of the centrifuged specimen is independent of the length of the specimen, it follows that the average water content of a specimen will decrease with increasing length of that specimen. This is in accordance with the results quoted on p 726.

Evaluation of A(ω).

If it could be assumed that the porous body is saturated at the outer face (distant a from the axis of the centrifuge) it would follow that $h = 0$ when $r = a$ and hence that

$$A(\omega) = \frac{\omega^2 a^2}{2g}.$$

Veihmeyer, Israelson and Conrad,[6] admitting the experimental difficulties in their work on soils, were only able to conjecture from their observations that " it is probable that the outer layer of the fine-textured soils is saturated, or nearly so," but, as they themselves suggest, the evidence presented cannot be regarded as conclusive.

Consequently, the above formula for $A(\omega)$ has not been assumed; on the contrary, a value has been obtained from the results of the distribution experiments carried out at different speeds.

To evaluate $A(\omega)$, the mean water contents of the specimens were first plotted against the mean values $\bar{H}(\omega, r)$ of the function $H(\omega, r)$. The mean value of r^2 over a specimen with faces at distances r_1 and r_2 from the axis and width d (= 2·9 cm.) is

$$\frac{r_1^2 + r_1 r_2 + r_2^2}{3} + \frac{d^2}{12}.$$

Hence the mean value of $\bar{H}(\omega, r)$ (equation (5)) over the specimen is

$$\bar{H}(\omega, r) = \frac{\omega^2}{2g}\left\{\frac{r_1^2 + r_1 r_2 + r_2^2}{3} + \frac{d^2}{12}\right\} \quad . \quad . \quad . \quad (7)$$

From equation (4) the average pressure deficiency over the specimen is $A(\omega) - \bar{H}(\omega, r)$.

The calculated values of $\bar{H}(\omega, r)$ shown in Table I. for the three samples of stone A, B and C were plotted against the mean water contents and curves were drawn through the points pertaining to the same speed. An example is shown in Fig. 3. Since $\bar{H}(\omega, r)$ is defined as the average value of $H(\omega, r)$ for fixed speed ω, over a range of r, any one curve may be taken to represent the relation between water content W and $H(\omega, r)$ for a particular stone and a fixed ω. Further, it can be assumed that under the conditions of experiment the water content at any point is determined uniquely by the pressure deficiency at that point, *i.e.* by $A(\omega) - H(\omega, r)$.

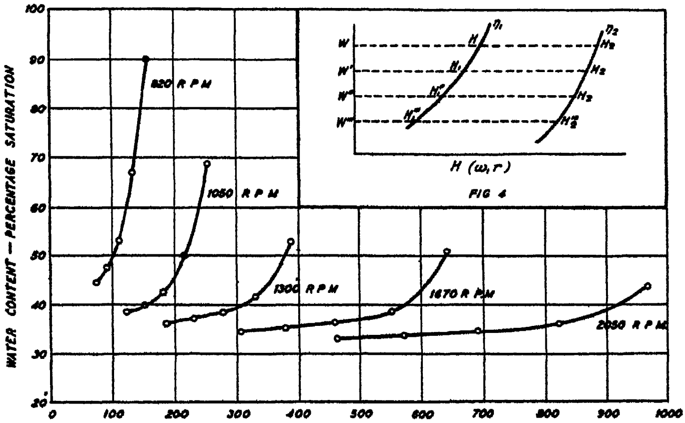

FIG 3 VARIATION OF WATER CONTENT WITH $\bar{H}(\omega r)$ AT 5 SPEEDS (STONE C)

On a curve (Fig. 4) for speed n_1 or angular velocity ω_1, let H_1, H_1', H_1'' . . . denote both the points and their abscissae and W, W', W'' . . . . . the corresponding water contents: the points on the curves for n_2 corresponding to the same water contents are H_2, H_2', H_2''. . . . .

Since the water content corresponding to point H_1 at speed n_1 is the same as that for point H_2 at speed n_2 we must have, in virtue of the above assumptions,

$$A(\omega_1) - H_1 = A(\omega_2) - H_2.$$

$$\therefore\ A(\omega_2) - A(\omega_1) = H_2 - H_1.$$

Similarly $$A(\omega_2) - A(\omega_1) = H_2' - H_1' = H_2'' - H_1'' = \text{etc.}$$

Hence any two curves relating to speeds n_1 and n_2 should be at a constant horizontal distance apart equal to $A(\omega_2) - A(\omega_1)$.

It is to be remembered that the *average* water content of a specimen may not always correspond exactly with its *average* pressure deficiency, that evaporation of water from the outer specimen could not be entirely prevented, and that it is difficult to draw an accurate smooth curve through five points, especially at the highest speeds where the curve becomes very flat. Nevertheless, the measured horizontal distances between pairs of curves, given in Table III., are reasonably constant.

TABLE III.—DISTANCES BETWEEN PAIRS OF CURVES MEASURED AT VARIOUS WATER CONTENTS.

	Water Content Per Cent. Total Saturation	$A(\omega_2) - A(\omega_1)$ $n_1 = 820$ $n_2 = 1050$	Water Content Per Cent Total Saturation.	$A(\omega_2) - A(\omega_1)$ $n_1 = 1050$ $n_2 = 1300$	Water Content Per Cent. Total Saturation.	$A(\omega_2) - A(\omega_1)$ $n_1 = 1300$ $n_2 = 1670$	Water Content Per Cent Total Saturation.	$A(\omega_2) - A(\omega_1)$ $n_1 = 1670$ $n_2 = 2050$
Stone A	96·0	122	95·0	147	90·0	323	85·0	351
	95·0	116	92·5	141	87·5	324	82·5	350
	94·0	110	90·0	139	85·0	323	80·0	351
	93·0	110	87·5	137	82·5	322	77·5	350
			85·0	136	80·0	321	75·0	351
			82·5	134	77·5	320	72·5	352
			80·0	131	75·0	319	70·0	353
					72·5	317	67·5	355
					70·0	318	65·0	357
							62·5	359
							60·0	368
							57·5	404
Mean		114		138		321		358
Stone B	95·0	124	87·5	173	82·5	269	72·5	372
	92·5	121	85·0	175	80·0	267	70·0	373
	90·0	117	82·5	175	77·5	265	67·5	378
	87·5	113	80·0	175	75·0	263	65·0	387
	85·0	113	77·5	176	72·5	264	62·5	395
	82·5	111	75·0	176	70·0	262		
			72·5	175	67·5	274		
			70·0	173	65·0	298		
Mean		117		175		271		381
Stone C	65·0	118	52·5	163	50·0	261	42·5	352
	60·0	116	50·0	161	47·5	261	40·0	347
	55·0	115	47·5	160	45·0	261	37·5	358
	50·0	116	45·0	160	42·5	260	35·0	395
	45·0	119	42·5	160	40·0	262		
			40·0	159	37·5	265		
Mean		117		160		262		363

For each stone the mean values of $A(\omega_2) - A(\omega_1)$ were plotted against $\omega_2^2 - \omega_1^2$. A linear relation was evident, indicating a general formula

$$A(\omega) = B + S\omega^2,$$

where S is the slope of the line. Substituting in equation (4),

$$h = B + S\omega^2 - H(\omega, r).$$

When $\omega = 0$, the stone is saturated and $h = 0$. Hence $B = 0$,

$$\textit{i.e.}\quad h = S\omega^2 - H(\omega, r),$$

or, from equation (5),

$$h = S\omega^2 - \frac{\omega^2 r^2}{2g},$$

which may be written

$$h = \frac{\omega^2}{2g}(c^2 - r^2) \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where $c = \sqrt{2gS}$ and is a constant length. The values of S were calculated by the method of least squares, and the values of c derived from them for the stones A, B and C were 6·88, 6·88, and 6·73 cm. respectively.

These values are closely similar to the radial distance a (= 6·77 cm.) of the edges of the composite block of specimens, parallel to and furthest from the axis of rotation and it would therefore appear that formula (8) could be written

$$^*h = \frac{\omega^2}{2g}(a^2 - r^2) \quad . \quad . \quad . \quad . \quad (9)$$

According to this formula the pressure deficiency vanishes at these edges, which implies that the stone is saturated there.

If the width of the specimen were negligible compared with the radial distance of the outer face, or if the outer face had been cylindrical and coaxial with the centrifuge, then it would follow that the whole of the outer face would be saturated.

In the theory it is assumed that the water is in hydrostatic connection throughout, and hence that the pressure deficiency varies continuously along the length of the specimen. The introduction of a grid in the experiment described above breaks the continuity in the water phase and in the pressure deficiency. From formulæ (9) and (7) the average pressure deficiency over a specimen extending from radii $(b - t)$ to b is

$$\frac{\omega^2}{2g}\left\{\frac{d^2}{6} + t\left(b - \frac{t}{3}\right)\right\}.$$

Hence the average pressure deficiency over the outer specimen of a composite block will decrease as the outer radius decreases and consequently the water content will increase. This affords an explanation of the fact that in Fig. 2 the water content of specimen 4′ is greater than that of 1′. Moreover, by calculating the average pressure deficiencies over the specimens 1′, 2′, 3′, 4′, 5′, using formula (9), a continuous relationship

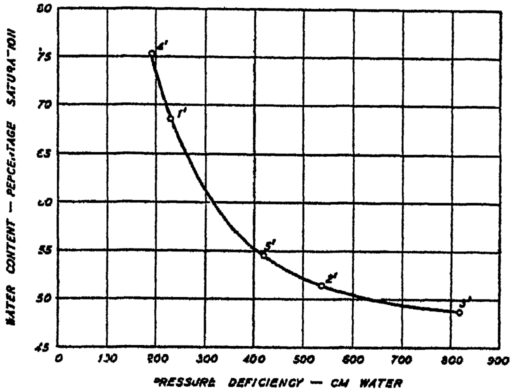

FIG 5 RELATION BETWEEN WATER CONTENT AND PRESSURE DEFICIENCY FOR SPECIMENS USED IN THE GRID EXPERIMENT

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* Using the concept of capillary potential [7, 8], Thomas [4] showed that $\psi_1 - \psi_2 = \frac{\omega^2}{2}(r_1^2 - r_2^2)$, where ψ_1 and ψ_2 are the capillary potentials at two points distant r_1 and r_2 from the axis. It is only possible to deduce from this that

$$\psi = -\frac{p}{\rho} = -\frac{\omega^2}{2}(a^2 - r^2)$$

if it is assumed that $\psi = 0$ both when $r = a$ and $p = 0$.

[7] E. Buckingham, *U.S. Dept. of Agric. Bureau of Soils. Bull.* No. 38, Washington, 1907, 28.

[8] W. Gardner, *Soil Sc.*, 1920, 10, 357.

between pressure deficiency and moisture content is at once obtained (Fig. 5).

The results of experiments, in which the speed of centrifuging was kept constant at 1300 rev. per min. and the position of the specimens relative to the axis of rotation varied, can now be considered. The values of $\bar{H}(\omega, r)$ shown in Tables I. and II. were plotted against the water contents of the specimens. The mean differences between curves at equal water contents were measured as before and appear in Table IV.

TABLE IV.

	Mean Differences between Curves.		
a_1	5·52 cm.	6·01 cm.	6·77 cm.
a_2	5·04 cm.	5·52 cm	6·01 cm.
Stone A . .	60	48	110
Stone B . .	49	51	117
Stone C . .	49	50	122
Expected values, $\frac{\omega^2}{2g}(a_1^2 - a_2^2)$.	48	53	91

From formula (9) the previous arguments show that the mean differences at equal water contents between any pair of curves should be constant: further, the differences should be equal to

$$\frac{\omega^2}{2g}(a_1^2 - a_2^2),$$

where a_1 and a_2 are the values of a corresponding to the two positions. The mean differences between curves for 2 and 3, and for 3 and 4 specimens agree fairly closely with the expected values; the curves for 4 and 5 specimens are rather too far apart. Since the possible sources of error mentioned in connection with the measurements of the distances between curves at different speeds apply also to these measurements, the general agreement is considered to be reasonably good and to give further support to the view that the formula

$$h = \frac{\omega^2}{2g}(a^2 - r^2),$$

can justifiably be used.

Comparison between Centrifuge and Hydrostatic Methods.

To compare the centrifuge and hydrostatic methods the equilibrium water contents of the specimens used in the centrifuge experiments have been determined by the hydrostatic method [9] at pressure deficiencies from zero to 563 cm. of water. Equilibrium was approached from the saturated condition. Thus both processes involve removal of water and and it can be assumed that hysteresis effects [9, 10, 11] will not need to be considered. The water contents of the five specimens of each of the 3 stones A, B, C were plotted against the corresponding pressure deficiencies. Freehand curves were drawn to fit as well as possible the points corresponding to each individual specimen. From the five curves for each stone a mean curve was calculated. The mean curves are shown in Fig. 6, together with the *individual* results obtained by the hydrostatic method. On the same figures are plotted the *mean* centrifuge water contents given in Table I., the mean pressure deficiencies being calculated from formulæ (7) and (9).

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[9] Report of the Building Research Board for the year 1931. London, 1932. H.M.S.O., pp. 21-23.

[10] W. B. Haines, *J. Agric. Sc.*, 1930, **20**, 97.

[11] L. A. Richards, *Physics*, 1931, **1**, 318.

The agreement between the hydrostatic and centrifuge curves for stone A over the range of pressure deficiencies investigated is not good, except perhaps at the end of the range, *i.e.* about 550 cm. For the other two stones the agreement is considerably better, especially from 250-550 cm. for stone B and from 100-550 cm. for stone C. The discrepancies between the hydrostatic and centrifuge curves over the sensitive range, where the curves are steepest, may be caused by the breakdown of one or both of the assumptions, which are fundamental to the theoretical discussion, namely that:—

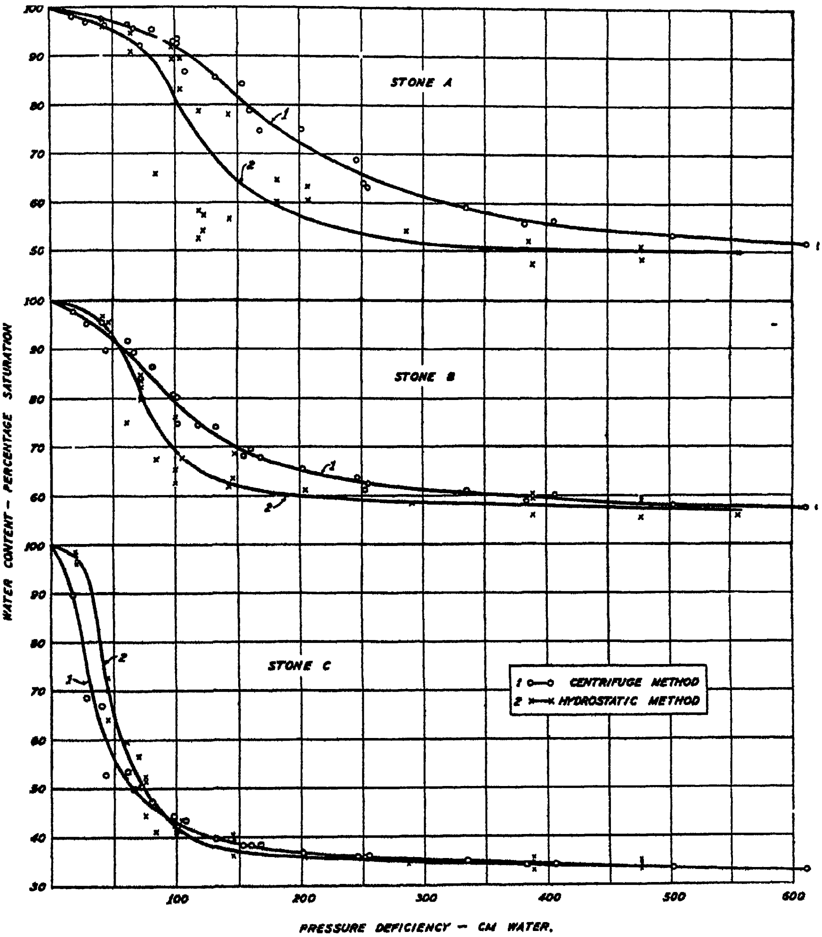

FIG. 6. VARIATION OF WATER CONTENT WITH PRESSURE DEFICIENCY.

(*a*) The hydrostatic pressure is continuous throughout the centrifuged specimen.

(*b*) The functional relation between water content and pressure deficiency is the same for the hydrostatic and centrifuge methods.

Summary.

1. Centrifuge experiments have been carried out on samples of Portland stone initially saturated with water.

2. The pressure deficiency at a point distant r from the axis of rotation is given by the equivalent height of water

$$h = A(\omega) - \frac{\omega^2 r^2}{2g},$$

where ω is the angular velocity. $A(\omega)$ is a constant for a given speed and for any one position of the specimen.

3. The formula affords an explanation of the observed moisture gradient along the radial length of centrifuged samples, and hence of the variation of mean water content with size of sample.

4. $A(\omega)$ could have been evaluated by assuming the outer surface to be saturated, but the experimental evidence hitherto advanced in support of this view was considered to be inadequate. Without making any such assumption the results of distribution experiments show that

$$A(\omega) = \frac{\omega^2 c^2}{2g},$$

where c is a constant length independent of ω.

5. The experimentally determined values of c indicate the general formula

$$h = \frac{\omega^2}{2g}(a^2 - r^2),$$

where a is the distance of the outermost points of the centrifuged specimen from the axis.

This formula implies that the specimen is saturated at these points and that, if the outer surface is a cylinder coaxial with the centrifuge, the whole of this surface is saturated.

6. A comparison is made between curves relating pressure deficiency with water content, as determined by the hydrostatic and centrifuge methods.

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Garston,
Herts.

ON THE THERMAL DECOMPOSITION OF ETHANE, ETHYLENE, ACETALDEHYDE, ETC.

By Morris W. Travers.

Received 9th February, 1937.

(1) Introduction.

During the past few years the rates of thermal decomposition of a number of simple compounds have been studied in this laboratory by the method of detailed analyses, which has been described in papers to which reference will be made. These investigations have led to the conclusion that in the case of a considerable number of compounds three stages are involved.

The first stage, which I refer to as the *background reaction*, may be represented by the equation,

$$A = B\,(+\,C) \qquad . \quad . \quad . \quad . \quad (1)$$

The second stage is the rate determining process, and is represented by

$$A + B = AB \qquad . \quad . \quad . \quad . \quad (2)$$

where AB is an unstable intermediate, which decomposes in a manner represented by

$$AB = D(+\,E + \text{etc.}) \qquad . \quad . \quad . \quad . \quad (3)$$

indicating that a single product, or two or more products, may result from a single activation process. The formation of an activated complex is not considered in this paper.

When the influence of the background reaction can be eliminated, the second stage involves a simple bimolecular reaction, but owing to the influence of the background reaction the process has generally a more complex character. The third stage involves rapid changes, so that the overall rate of reaction, involving the rate of disappearance of A + B, is measured by the total rate of formation of the products.

The proportions in which the products are formed is determined by conditions which may have no influence on the overall rate of reaction.

(2) The Thermal Decomposition of Ethane and of Acetaldehyde.

When ethane is heated to the neighbourhood of 600°, it is partially decomposed into ethylene and hydrogen, equilibrium in the system ethane-ethylene-hydrogen being approached very rapidly. This primary decomposition is accompanied by the formation of methane and a condensation product and, as was first shown by Travers and Hockin,[1] the rates for formation of both of these products show rapid acceleration, the *x-t* graphs bending towards the *x*-axis. However, after a short time, the rates of formation of both products slow down suddenly and simultaneously. It was also found that these phenomena did not occur in the case of experiments carried out with ethane-ethylene-hydrogen equilibrium mixtures.

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[1] Travers and Hockin, *Proc. Roy. Soc., A*, 1932, 136, 1.

The investigation was continued by Travers and Pearce,[2] who put forward the following explanation of the formation of methane and condensate (R) from the equilibrium mixtures, the assumption being made that hydrogen was always present, and that the observed rate of formation of condensate related to some early stage in a series of reactions, such as the formation of a C_4-complex. The rates of the processes were expressed by,

$$dR/dt = K_{cond}(C_2H_4)^2, \text{ and} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$d(CH_4)/dt = K_{me}(C_2H_4)(C_2H_6 + CH_4 + H_2) \quad . \quad . \quad (5)$$

That is to say, the condensate results from binary collision of ethylene molecules, while methane results from the binary collision of ethylene molecules with any other species of light molecule which may be present.

The value of K_{cond} was fairly constant throughout series of experiments at constant initial $C_2H_6 + C_2H_4$ concentration, but varied considerably with change in the initial concentration. The value of K_{me} varied with the hydrogen concentration. It was shown that the addition of methane to an equilibrium mixture did, at first, increase the rate of formation of methane, but that further addition reduced the rate. However, it was found that the initial rate of formation of condensate from pure ethylene was very slow, instead of being very fast (p. 749), and the explanation did not account for the fact that the two processes seemed to be related.

Since this work was completed, the results of the experiments of Seddon and Travers[3] on the thermal decomposition of acetaldehyde has suggested an alternative explanation of these phenomena. It was found that when acetaldehyde decomposes in an empty silica tube the main reaction is represented by,

$$CH_3CHO = CH_4 + CO \quad . \quad . \quad . \quad . \quad (6)$$

while in a packed tube the main reaction is represented by

$$2CH_3CHO = CH_3CH : CH_2 + CO\ H_2O \quad . \quad . \quad . \quad (7)$$

However, the overall rate of decomposition of acetaldehyde is independent of whether the tube is packed or not. The process has been referred to as one in which *paired products* result from a single activation process.[4] At the same time it was suggested that the decomposition process may be preceded by a *background reaction*, which in the case of acetaledhyde might be represented by

$$CH_2CHO \rightleftharpoons CH_2 : CHOH \quad . \quad . \quad . \quad . \quad (8)$$

the main reaction being initiated by binary collision, involving one of each species of molecule. It will readily be seen that such an explanation might be used to account for the acceleration observed in the thermal decomposition of acetaldehyde.

(3) Method of Investigation.

In the whole of the experiments now referred to, the method of detailed analyses was employed. A measured quantity of the gas to be investigated was introduced into a silica glass reaction tube, which was then sealed. The tube was then heated for a definite time, after which the contents were analysed.

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[2] Travers and Pearce, *J. Soc. Ch. Ind.*, 53, 321.

[3] Seddon and Travers, *Proc. Roy. Soc.*, *A*, 1936, 156, 234.

[4] Travers, *Nature*, 137, 906; 138, 967.

(4) Units Employed.

The results are expressed in gram atoms of carbon or hydrogen per litre (g.a.l.), or in gram mols. per litre (g.m.l.); in the latter case the quantity of condensate is given as the number of mols of C_2-hydrocarbon changed. The hour is the unit of time, unless it is stated otherwise.

(5) Ethane-ethylene-hydrogen Equilibrium Mixtures.

From the results of the experiments with acetaldehyde it seemed probable that the methane and condensate produced during the pyrolysis of the hydrocarbons might be formed as *paired products* of a single activation process. I therefore decided to re-examine the experimental results obtained in the previous investigations. I found that the rate of formation of methane and condensate together, from the experiments of which the essential details are given in Table I., could be represented by the formula,

$$d(CH_4 + R)/dt = K_1(C_2H_6)(C_2H_4) \quad . \quad . \quad . \quad (9)$$

and since we are working within the range in which equilibrium, represented by

$$k = (C_2H_4)(H_2)/(C_2H_6) \quad . \quad . \quad . \quad (10)$$

is established very rapidly, we also find the relationship

$$d(CH_4 + R)/dt = K_2(C_2H_4)^2(H_2) \quad . \quad . \quad . \quad (11)$$

so that

$$K_1 = K_2k \qquad (12)$$

Equations (11) and (12) have no physical significance, but the application of them makes it possible to make use of all available data.

It is not, of course, possible to apply continuous methods to the evaluation of the constants, but writing the equations,

$$K_1 = (CH_4 + R)/\Sigma(C_2H_6)(C_2H_4)t \quad . \quad . \quad (13)$$
$$K_2 = (CH_4 + R)/\Sigma(C_2H_4)^2(H_2)t \quad . \quad . \quad . \quad (14)$$

the following method of computation was used. The concentrations of the ethane, ethylene, and hydrogen, and the squares of the ethylene concentration, were plotted against the time. Then, when the quantity of methane and concentrate for any time interval is given by $(CH_4 + R)$, the areas below the graphs, divided by the time interval, are the quantities in brackets in the denominators. The results are set down in Table I.

The results are summarised in Table II. Here the values of log K_1 and log K_2k are expressed in gram mols. per litre, obtained by adding log 2 to the mean values in Table I., Column 7 and log $(k_{atm.} \times 4 \times 273)/(22{\cdot}4 \times T)$ to the values in Table I., Colunm 8. The values of $k_{atm.}$ are to be found in Table X.[3], and the accuracy of the data is checked by the theoretical work of Teller and Topley.[5]

It may be pointed out here that, besides the difficulties involved in introducing the exact quantities of the equilibrium mixtures into the reaction tubes, each of the experimental points was determined by analyses involving the estimation of hydrogen, methane, ethane, and ethylene, the condensate being the difference between the sums of several large quantities. Experimental error may therefore account for many of the irregularities observed in the work. However, the results as a whole appear to justify the general argument which I am now advancing; though, considering the importance of knowledge of the thermal changes in hydrocarbon systems, which must be based on information relating to ethane and ethylene, it would be worth while extending this investigation, making use of the experience gained in the conduct of many similar researches.

[5] Teller and Topley, *J. Chem. Soc.*, 1935, 876.

TABLE I—DATA IN GRAM ATOMS OF CARBON OR HYDROGEN PER LITRE. SERIAL LETTERS AND NUMBERS RELATE TO EXPERIMENTS BY TRAVERS AND PEARCE.[2]

1. Serial.	2. Temp. (°C.).	3. Initial Concentration	4.	5.	6.	7 log K_1.	8 log K_2
		$C_2H_6+C_2H_4$.	C_2H_6.	C_2H_4.	H_2.		
A1 a	620	0·08	0·06994	0·01006	0·00840	1·7610	4·6248
b						1·8299	4·6426
c						1·8681	4·6485
Mean						1·8197	4·6386
B1 a	620	0·05	0·03871	0·01129	0·00410	1·9073	4·7379
b						1·8383	4·7760
B2 a			0·04186	0·00814	0·00616	1·7836	4·7107
b						1·8027	4·7252
c					0·00	—	4·7385
B3 a			0·04363	0·00637	0·00800	1·8371	4·7574
b						1·7737	4·7011
B4 a			0·04478	0·00523	0·01000	1·7662	4·6794
b						1·7059	4·6251
B5 a			0·04690	0·00310	0·01800	1·8590	4·6697
b						1·8104	4·5784
Mean						1·8084	4·6990
C1 a	620	0·03	0·02610	0·00390	0·00800	1·6656	4·7443
b						1·6473	4·7232
C2 a			0·02792	0·00209	0·01575	1·6143	4·6923
b						1·6306	4·7156
Mean						1·6394	4·7188
D1 a	620	0·02	0·01540	0·00460	0·00408	1·6282	4·7140
b						1·6692	4·7523
c						1·7047	4·7258
D2 a			0·01743	0·00257	0·00806	—	4·6486
b						—	4·7206
c						—	4·7273
D3 a			0·01861	0·00139	0·01510		4·7184
b							4·6845
Mean						1·6674	4·7111
E1 a	610	0·08	0·06625	0·01375	0·00580	1·6408	4·6002
b						1·8213	4·6848
c						1·7185	4·6705
E2 a			0·07185	0·00815	0·01125	1·7029	4·6393
b						1·5853	4·5125
Mean						1·6950	4·6233
F1	610	0·05					
F2 a			0·04496	0·00504	0·00880	1·6885	4·7058
b						1·7056	4·7124
Mean						1·6970	4·7091
G1 a	590	0·08	0·07034	0·00966	0·00500	1·3614	4·5329
b						1·3916	4·5933
c						1·3569	4·5420
d						1·3993	4·5543
G2 a			0·07332	0·00668	0·00792	—	—
b						—	—

TABLE I.—*Continued*

1.	2.	3.	4.	5.	6.	7.	8.
Serial.	Temp. (°C.).	Initial Concentration.				log K_1.	log K_2.
		$C_2H_6+C_2H_4$	C_2H_6.	C_2H_4.	H_2.		
G3 a			0·07660	0·00340	0·01450	1·3362	4·5388
b						1·2981	4·4505
c						1·3715	4·5198
d						1·3939	4·5596
Mean						1·3636	4·5339
H1 a	590	0·05	0·04175	0·00825	0·00350	1·4175	4·5634
b						1·4219	4·5620
c						—	4·5744
H2 a			0·04326	0·00674	0·00445	1·5033	4·5544
b						1·4562	4·4410
c						1·4340	4·4279
H3 a			0·04456	0·00544	0·00540	1·3187	4·5325
b						1·3582	4·5327
c						1·3479	4·5216
d						1·3441	4·5170
e						1·3402	4·5127
H4 a			0·04550	0·00450	0·00675	1·3515	4·6307
b						1·3636	4·5224
c						1·3499	4·5274
d						—	4·5191
e						—	4·5112
H5 a			0·04626	0·00374	0·00815	1·2966	4·4799
b						1·2537	4·4467
H6 a			0·04688	0·00312	0·01005	1·3287	4·4752
b						1·3026	4·3612
c						—	—
d						1·2984	4·4535
H7 a			0·04736	0·00264	0·01215	1·3451	4·5294
b						1·3256	4·4850
c						1·3430	4·4921
d						1·3391	4·4976
H8 a			0·04774	0·00226	0·01420	1·3260	4·4588
b						1·3139	4·4509
H9 a			0·04821	0·00179	0·01785	1·3858	4·5888
H10 a			0·04864	0·00136	0·02400	1·3942	4·5703
b	(3 h)					1·4101	4·6031
H11 a			0·04882	0·00118	0·02750	1·3306	4·7624
b	(3·5 h)					1·3348	4·7438
Mean						1·3564	4·5262
I1 a	590	0·025	0·02124	0·00376	0·00382	1·3725	4·5534
b						1·3683	4·5476
c						1·3455	4·6289
d						1·4212	4·5870
e						1·4336	4·5958
Mean							
J1 a	570	0·05	0·04679	0·00321	0·00590	0·8597	4·3696
b						0·7911	4·4116
c						—	4·3656
J2 a			0·04803	0·00197	0·01000	0·9909	4·3676
b						0·9446	4·3409
Mean						0·8966	4·3711
K1 a	550	0·05	0·04176	0·00824	0·00154	0·8552	4·3977
b						0·9008	4·4729
c						0·9243	4·4961
Mean						0·8934	4·4556

TABLE II.—GRAM MOLS PER LITRE.

Temp °C	Serial	Initial $C_2H_6 + C_2H_4$.	log k	log K_1.	log K_2k.
620	A	0·04	1·7844	2·1207	2·0250
	B	0·025		2·1004	2·0850
	C	0·015		1·9404	2·1052
	D	0·01		1·9684	2·0078
	Mean			2·056	2·085
610	E	0·04	1·6034	1·9960	1·8287
	F	0·025		2·0015	1·9090
	Mean			1·999	1·859
590	G	0·04	1·5373	1·6646	1·6732
	H	0·025		1·6574	1·6055
	I	0·0125		1·6872	1·6398
	Mean			1·662$_5$	1·653
570	J	0·025	4·3615	1·107$_5$	1·334$_5$
550	K	0·025	1·0790	1·194	1·136$_6$

If the mean values of log K_1 and log K_2k are plotted against $1/T$, the points are found to be distributed about a line from the slope of which 48·5 K. cals. is obtained for E (Fig. 3).

However, further study of the data shows that the mean values for the sub-series exhibit systematic variation with other factors. I have taken the data for the two long series B1 to B5 at 620° and H1 to H11 at 590°, and in Table III. I have set down the values of log K_1, log K_2k, and mean log K for the sub-series against figures which indicate the initial rates of

TABLE III.—INITIAL CONCENTRATION $C_2H_6 + C_2H_4$ 0·05 GRAM ATOMS CARBON PER LITRE.

T °C.	Serial.	log K_1.	log K_2k.	Mean log K.	Δt Hour).	ΔH_2.	ΔC_2H_4.	ΔC_2H_6.	ΔCH_4.	ΔR.	$\Delta_2 CH_4 - R$.
620	B 1	2·1738	2·1432	2·1585	0·25	+ 0·00072	0·00318	0·00262	0·00258	0·00308	0·00566
	B 2	2·0941	2·1112	2·1026	0·25	+0·00066	0·00125	0·00332	0·00246	0·00212	0·00458
	B 3	2·1064	2·1156	2·1110	0·25	+0·00005	0·00031	0·00330	0·00240	0·00117	0·00357
	B 4	2·0320	2·0386	2·0353	0·25	+ 0·00023	0·00015	0·00290	0·00222	0·00083	0·00305
	B 5	2·1269	2·0354	2·0811	0·25	−0·00089	-0·00001	−0·00202	0·00164	0·00038	0·00202
590	H 1	1·7207	1·8060	1·7133	1·00	+0·00094	−0·00293	- 0·00377	0·00361	0·00354	0·00715
	H 2	1·7655	1·6138	1·6896	1·00	+0·00072	−0·00150	-0·00437	0·00298	0·00280	0·00578
	H 3	1·6426	1·6683	1·6554	1·00	+0·00032	-0·00082	−0·00391	0·00276	0·00204	0·00480
	H 4	1·6560	1·6816	1·6688	1·00	+0·00008	−0·00040	−0·00404	0·00304	0·00140	0·00444
	H 5	1·5761	1·5027	1·5394	1·00	−0·00068	−0·00004	−0·00324	0·00238	0·00090	0·00328
	H 6	1·6109	1·5693	1·5901	1·00	−0·00050	+0·00007	−0·00310	0·00209	0·00096	0·00305
	H 7	1·6392	1·6404	1·6365	1·00	−0·00085	+0·00021	- 0·00388	0·00230	0·00070	0·00300
	H 8	1·6209	1·5942	1·6075	1·00	−0·00135	+0·00025	−0·00245	0·00190	0·00030	0·00220
	H 9	1·6868	1·7282	1·7075	1·00	−0·00153	+0·0005	−0·00180	0·00170	0·00000	0·00170
	H 10	1·7031	1·7261	1·7146	1·00	−0·00120	0·00000	−0·00160	0·00160	0·00000	0·00160
	H 11	1·6416	1·8169	1·7342	1·00	0·001	+0·00008	- 0·00225	0·00233	0·00000	0·00233

change in concentration of the constituents of each equilibrium mixture. The graphs in Figs. 1 and 2 show at once the rate of change of hydrogen concentration with time, and the relationship between mean log *K* and the initial hydrogen concentration.

It was to be expected that the effect of the operation of the process represented by

$$C_2H_6 \quad C_2H_4 + H_2 \quad . \quad . \quad . \quad (15)$$

which we have called the *background reaction*, by which equilibrium is maintained in the system, which is shown to have a marked influence on the rate of formation of methane and condensate from pure ethane, particularly at the lower temperatures, cannot be entirely without influence in the case of the equilibrium mixtures, again particularly at the lower temperatures. The data in Table III. and in Figs. 1 and 2 show that while mean log *K* varies but little in Series B, systematic variation is found in Series H. In this series the values of mean log *K* diminish while the rate of reaction, measured by the values of $\Delta(CH_4 + R)$, also diminishes from H1 to H4-5, and increase as the rate at which hydrogen is taken up in the process involved in the formation of methane from the complex formed by collision of ethane and ethylene molecules also increases. Both these processes involve the adjustment of equilibrium in the ethane-ethylene-hydrogen system by the operation of the background reaction, a measure of the effect of which is the rate of change in the hydrogen concentration. When this reaches a minimum, mean log *K* has also a minimum value.

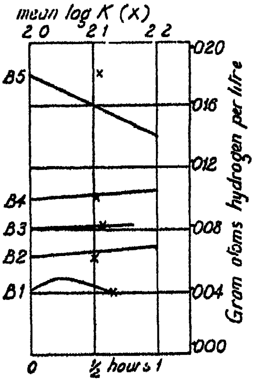


FIG. 1.

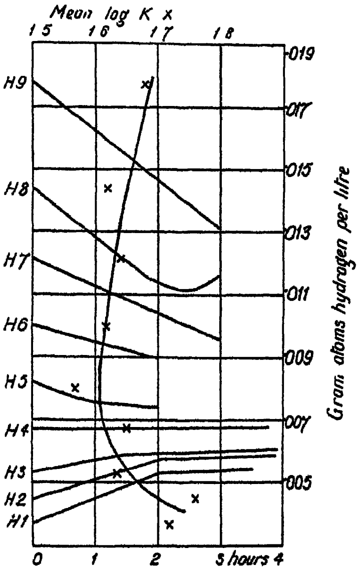


FIG. 2.

If we take the limiting values of mean log *K* to be 2·08 at 620° and 1·61 at 590°, and plot these figures against $1/T$ (Fig. 3), we find that the values for mean log *K* (Table II.) obtained from the Series E and F at 610°, and J at 570° lie very close to the graph passing through the points corresponding to 620° and 590°. Reference to the paper by Travers and Pearce[2] (Table I.) or to Table III. will show that in these series the variation of hydrogen concentration with time is relatively small.

From this graph the value of E is found to be 55 K.cals. The interpolated values for mean log K are now (Table IV):

TABLE IV.

T° C.	Mean log K (g.m l.).
620	2·08
610	1·925
600	1·77
590	1·61
580	1·445
570	1·275
550	0·92

TABLE V

Initial Concentration of $C_2H_6 + C_2H_4$ in gram mols. litre.	Mean log K 620° gram mols. litre.
0·04	2·08
0·025	2·08
0·015	2·005
0·01	2·065

Since at the highest temperature it is clear that the rate of formation of methane and condensate is little affected by the operation of the background reaction, the data in Table V. lend valuable support to the theory which I have put forward.

The data for 590° have been applied to the calculation of the relationship between the rate $d(CH_4 + R)/dt$ and the number of effective collisions deduced from the Maxwell Distribution Law. Taking the above value for log K the value in molecules per c.c. per hour is given by

$$\log K = 1{\cdot}61 + \log (6{\cdot}06 \times 10^{20}) = 22{\cdot}392 \quad . \quad . \quad (16)$$

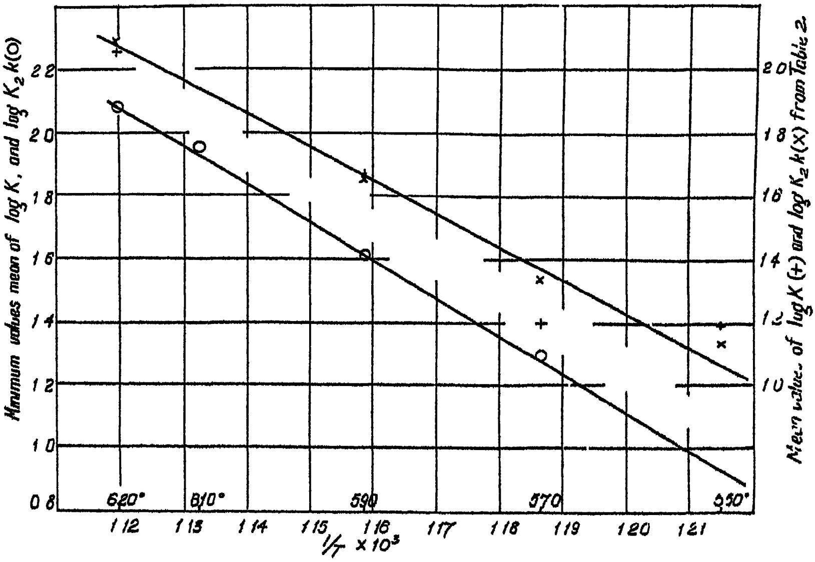


FIG. 3.

and from the Maxwell Distribution Law for bimolecular collisions between ethane and ethylene,

$$\log K = \log[3600\sqrt{2\pi\sigma^2}\sqrt{(\bar{u}_1^2 + u_2^2)}\; n_1 n_2 e^{-55000/1{\cdot}98 \times 868}] = 22{\cdot}970 \quad (17)$$

where σ for both kinds of molecules is $3{\cdot}78 \times 10^{-8}$. This leads to the result that one effective collision in four is fruitful. If one takes 1·668 (Table II.) the mean value of log K for the experiments at 590° and 48·3 for the value of E, this number is increased to 130. In the case of the formulæ proposed by Travers and Pearce,[2] the value of p was nearly 1/10,000, so that this calculation supports the explanation which I now put forward.

The simplest explanation which can be given to the facts is the following. From a mixture of ethane, ethylene, and hydrogen, initially in equilibrium, and undergoing thermal change so that the readjustment of equilibrium through the operation of equation No. 15 is small, the formation of methane and condensate arises from a single bimolecular process initiated by collision of ethane and ethylene molecules. The energy of activation is 55 K. cals., and a large proportion of the effective collisions are fruitful. Fruitful collisions lead to the formation of a bimolecular unstable complex, and it is the rate of formation of this complex which we measure. We have no information as to the conditions which determine the decomposition of the complex, with or without reaction with hydrogen, to form methane and condensate. The reaction appears to be one in which *paired products* result from a single activation process.

(6) The Thermal Decomposition of Pure Ethane.

The essential data relating to three series of experiments at 590°, and at an initial concentration of 0·025 g.m.l., are set down in Table VI. In all three series thick walled silica tubes were used. In Series A the tubes were pretreated with hydrogen, in Series B this was not done, and in Series C the tube was packed with capillary silica tubes. The $(CH_4 + R)/t$ graphs are shown in Fig. 4. In the case of Series A and B the rate $d(CH_4 + R)/dt$ is strongly accelerated, and the acceleration continues up to the break point. It will also be noticed that the value of the ratio $P_{C_2H_4}P_{H_2}/P_{C_2H_6}$ never approaches very close to the equilibrium value 0·0244. In Series C the form of the $(CH_4 + R)/t$ graph appears to be practically identical with those obtained in experiments with equilibrium mixtures, and the value of the ratio $P_{C_2H_4}P_{H_2}/P_{C_2H_6}$ approaches the equilibrium value very quickly. Now we can calculate from the values of the ethane and ethylene concentration, using equation No. 9, the values of $d(CH_4 + R)/dt$, and also determine the actual values from the graphs in Fig. 4. The values are given in Table VI., lines 4 (observed) and 5 (calculated), the results being plotted against the time in Fig. 5. The graphs for A and B show the calculated rate increasing at first and then decreasing, while the observed rate increases at first more slowly and then more rapidly than the calculated values, reaches a maximum, and then falls suddenly to near the calculated rate. It appears to increase again after the break point; but the evidence that it does so is only semi-quantitative. In the case of

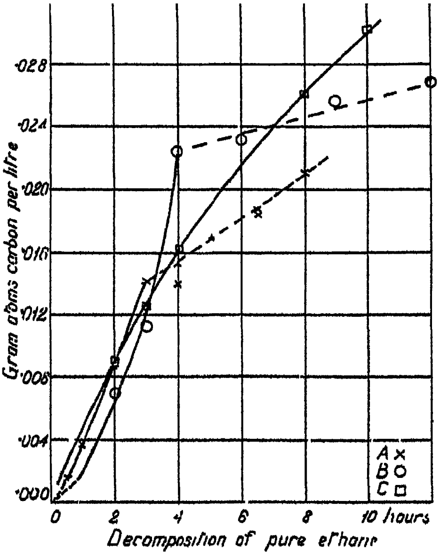
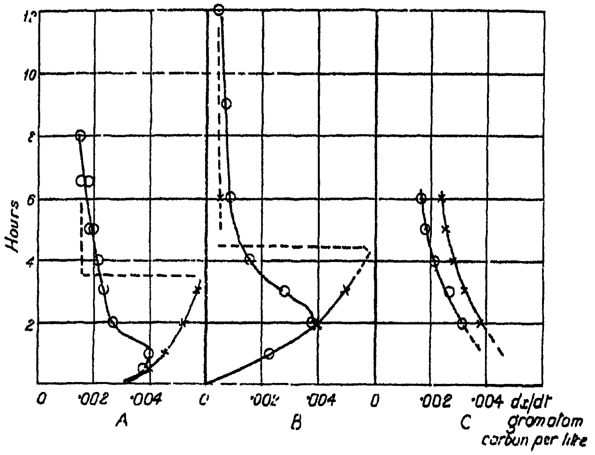


FIG. 4.

Series C, the observed rate is greater than the calculated rate, but it never becomes much greater and the rates diminish together.

The fact that the observed rate, $d(CH_4 + R)/dt$, is greater than the calculated rate, $K(C_2H_6)(C_2H_4)$, may be accounted for qualitatively by the same mechanism as has been put forward in the case of the equilibrium mixtures, as the difference increases with increase in the value of the product $(C_2H_6)(C_2H_4)$. However, in the case of the packed tube (C) the background reaction is mainly a surface reaction, and the difference tends to disappear. Also, in this case, since it is impossible to experiment in the region where the difference is most marked, the effect tends to disappear.



× Found. ⊙ Calculated.

FIG. 5.

TABLE VI.—TEMPERATURE 590°. INITIAL $C_2H_4 + C_2H_6$ 0·05 GRAM ATOM CARBON PER LITRE.

Time (hours).	½	1	2	3	4	4	5	5	6·5	6·5	8
$CH_4 + R$	0·00166	0·00372	0·00907	0·01388	0·01620	0·01412	0·01698	0·01486	0·01856	0·01666	0·02112
H_2	0·00466	0·00542	0·00596	0·00544	0·00599	0·00602	0·00584	0·00572	0·00594	0·00578	0·00620
C_2H_4	0·00416	0·00452	0·00354	0·00334	0·00316	0·00322	0·00286	0·00308	0·00262	0·00312	0·00282
$d(CH_4 + R)/dt$	0·00398	0·00456	0·00522	0·00565	—	—	—	—	—	—	—
$K(C_2H_6)(C_2H_4)$	0·00375	0·00395	0·00264	0·00239	0·00201	0·00215	0·00180	0·00200	0·00151	0·00180	0·00176
$P_{C_2H_4} \times P_{H_2}/P_{C_2H_6}$	0·0153	0·0207	0·0198	0·0196	0·0210	0·0206	0·0196	0·0195	0·0174	0·0180	0·0237

	B							C				
Time (hours)	2	3	4	6½	9	12	12	2	3	4	5	6
$CH_4 + R$	0·00702	0·01132	0·02224	0·02314	0·02556	0·02585	0·02684	0·00905	0·01265	0·01600	0·01880	0·02125
H_2	0·00440	0·00490	0·00441	0·00472	0·00468	0·00494	0·00508	0·00585	0·00610	0·00610	0·00610	0·00611
C_2H_4	0·00480	0·00396	0·00302	0·00248	0·00238	0·00208	0·00222	0·00415	0·00385	0·00350	0·00310	0·00275
$d(CH_4 + R)/dt$	0·00396	0·00410	—	—	—	—	—	0·0038	0·0035	0·0030	0·0027	0·0023
$K(C_2H_6)(C_2H_4)$	0·00383	0·00281	0·00156	0·00124	0·00107	0·00093	0·00095	0·0036	0·0030	0·0025	0·0021	0·0016
$P_{C_2H_4} \times P_{H_2}/P_{C_2H_6}$	0·0190	0·0198	0·0193	0·0170	0·0179	0·0166	0·0191	0·0234	0·0248	0·0249	0·0238	0·0230

Excluding the question of a chain mechanism for a moment it is possible to account for the enhanced rate in the case of pure ethane in the following way. The activation energy[6] of the primary decomposition process is about 70 K.cals., while the requirements of the process are 30 K cals. Hence, about 40 K.cals. remains to be dissipated. So long as the system does not reach equilibrium, the energy distribution amongst the ethylene molecules must be at a higher average than the normal, so that the probability of fruitful collision with an ethane molecule is increased. When the reaction tube is packed, the primary decomposition process is, to a considerable extent, a wall reaction, and the energy is dissipated at the surface.

This does not, however, account for the fact that sometimes, in a series of experiments, observations are recorded which are represented by points on a graph in continuation of the initial portion of the $x - t$ graph, which show that the acceleration is sometimes continued long after equilibrium in the ethane-ethylene-hydrogen system has been reached. Travers and Pearce[2] give details of a series of experiments in which this occurs (p. 333). This phenomenon cannot be explained except on the assumption that a chain mechanism operates in the gas phase.

The phenomena associated in the break point, which is accompanied by a sudden fall in the hydrogen concentration, will be considered later.

At higher temperatures, the high temperature coefficient of the primary decomposition process would lead one to expect that equilibrium in the system ethane-ethylene-hydrogen would be established very rapidly. This is the case at 620° and the ratio $P_{CH_4} \times P_{H_2}/P_{C_2H_6}$ quickly reaches the equilibrium value 0·0446 (atm.). In a series of experiments with initial concentration 0·025 g.m.l., the break in the $(CH_4 + R)/t$ graph is not very obvious.

TABLE VII.—EXPERIMENTS WITH PURE ETHANE AT 620°.

Data in Gram Atoms Carbon per Litre.

Time (hours).	0·5.	0·67.	1·0.	1·5,	2.	2·75.
$(CH_4 + R)$	0·01075	0·01339	0·01656	0·02232	0·02500	0·02887
H_2	0·00761	0·00784	0·00763	0·00760	0·00756	0·00747
C_2H_4	0·00543	0·00582	0·00488	0·00397	0·00372	0·00320
$d(CH_4 + R)/dt$ graph	0·00200	—	0·0105	0·0085	0·0060	--
$K(C_2H_6)(C_2H_4)$	0·0115	0·0108	0·0085	0·0056	0·0048	—
$Pc_2H_4 \times PH_2/Pc_2H_6$	0·0443	0·0547	0·0477	0·0649	0·0484	0·0505

The break lies at between 0·5 and 1 hour, when the observed rate falls from 0·0200 to 0·0105, and there is a drop in the hydrogen concentration.

(7) The Similarity in the Behaviour of Ethane, Acetaldehyde, and other Compounds. The Unstable Intermediates.

When acetaldehyde decomposes thermally, two processes take place, represented by equations Nos. 6 and 7. The first predominates in empty tubes, the second in a packed tube; but the actual rate of decomposition of the acetaldehyde is independent of whether the tube is packed or not. This is a case in which *paired products* seem to result from a single activation process, probably through the sensibly irreversible formation of an unstable intermediate.

The fact that the decomposition of acetaldehyde is self-accelerated may be accounted for by assuming that the decomposition process is preceded by a *background* reaction possibly represented by

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[6] Marce and McCluer, *J. Ind. and Eng. Ch.*, 1931, 878.

$$CH_3 . CHO \rightleftharpoons CH_2 . CHOH \quad . \quad . \quad . \quad (18)$$

and that the main reaction is initiated by binary collisions involving the two species of molecule. If equilibrium at air temperature lies over on the left-hand side of the equation the initial rate will be very small, and the rate will increase with the values of the product

$$(CH_3 . CHO) \times (CH_2 : CHOH).$$

Again, the process shows evidence of chain mechanism which must originate in the operation of the *background reaction*. This appears to operate in the gas phase for the only effect of packing the tube is to increase the formation of propylene. Unfortunately, it is not possible to start with equilibrium mixtures, as in the case of the hydrocarbon; and indeed, the hydrocarbons furnish the only case in which the background reaction can be studied independently. Unfortunately, the primary decomposition of the hydrocarbons is influenced by surface, which makes the problem much more difficult to study.

In the case of acetaldehyde, the proportion in which the products are obtained is determined only by surface. It can be supposed that the unstable intermediate has a life, Δt, and if before this period the complex does not make effective contact with the surface it decomposes according to equation (6). If within this period it makes effective contact, it decomposes in accordance with equation (7). The size of the tube and the mean free path do not appear to be controlling factors, for the state of the surface is also important.

The formation of paired products is not a necessary characteristic of reactions of this type. Acetone, which is being studied by A. C. Carter, yields only methane and ketene, the reaction being self-accelerated, as in the case of acetaldehyde. Surface does not affect the rate of this reaction.

The factor which determines the products of decomposition of the $(C_2H_6)(C_2H_4)$ complex seems to be hydrogen, since the ratio CH_4/R increases with hydrogen concentration. It seems likely that the limiting value of the ratio tends, in one direction, to approach

$$n(C_2H_6)(C_2H_4) = 2n\ CH_4 + (C_2H_2)_n \quad . \quad . \quad . \quad (19)$$

that is, the complex does not lose hydrogen, except as methane. An analogous case which has been studied by P. A. Bosanquet, C. G. Silcocks, and A. F Wilshire in this laboratory is the decomposition of methyl amine, which appears to follow alternative routes

$$CH_3NH_2 = HCN + 2H_2 \quad . \quad . \quad . \quad (20)$$

$$CH_3NH_2 + H_2 = CH_4 + NH_3 \quad . \quad . \quad . \quad (21)$$

However, the rate of reaction No. 21 never exceeds the rate of reaction No. 20, but may be equal to or less than it, and is unaffected by adding hydrogen to the methyl amine. The case is exactly the opposite to that of the hydrocarbons; for while the complex $(C_2H_6)(C_2H_4)$ does not lose hydrogen spontaneously, the complex $(CH_3NH_2)_2$ does not take up hydrogen spontaneously.

(8) The Form of the x/t Graphs.

According to Semenoff,[7] the rates of most reactions involving chain mechanisms can be represented by the equation,

$$x = e^{\phi t} \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

the graphs obtained by plotting log x against t being linear. This relationship seems, however, to apply only in cases in which the energy change is considerable, where the rate of formation of primary centres is small, in so far as the distinction can be made, and the process is carried forward almost entirely through the formation of secondary centres.

TABLE VIII.*

Temperature.	Initial $(CH_2)_2O$.	a.	n.	$t_{\frac{1}{2}}$.
Ethylene Oxide.				
420°	0·02885	$6{\cdot}4 \times 10^{-6}$	2·41	24·5
400°	0·01573	$3{\cdot}0 \times 10^{-6}$	1·95	60
400°	0·02885	$5{\cdot}5 \times 10^{-6}$	1·91	62
400°	0·03981	$7{\cdot}25 \times 10^{-6}$	1·92	61
380°	0·02885	$3{\cdot}4 \times 10^{-6}$	1·62	174
Acetaldehyde.				
500° *c*	0·07464	$4{\cdot}17 \times 10^{-3}$	1·24	5·8
500° *c*	0·05004	$1{\cdot}85 \times 10^{-3}$	1·24	8·5
500° *c*	0·02592	$0{\cdot}67 \times 10^{-3}$	1·24	10·5
500° *c*	0·01463	$0{\cdot}30 \times 10^{-3}$	1·24	11·0
500° *c*	0·00934	$0{\cdot}20 \times 10^{-3}$	1·24	11·0
420° *a*	0·02507	$8{\cdot}9 \times 10^{-5}$	1·66	20
400° *b*	0·04750	$2{\cdot}56 \times 10^{-4}$	1·24	39
400° *b*	0·04220	$2{\cdot}10 \times 10^{-4}$	1·24	40
400° *b*	0·03270	$1{\cdot}53 \times 10^{-4}$	1·24	43
400° *b*	0·02607	$1{\cdot}14 \times 10^{-4}$	1·24	46
400° *b*	0·02507	$1{\cdot}39 \times 10^{-4}$	1·18	46
380° *a*	0·02507	$1{\cdot}12 \times 10^{-4}$	0·97	118
360°	0·12507	$0{\cdot}67 \times 10^{-4}$	0·97	219

* Data from paper by Seddon and Travers.[3]

In the case of the reactions which we are considering, a linear relationship is generally obtained by plotting log n against log t, so that

$$x = at^n \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

represents the amount of the compound changed in time t, n appears to be dependent on the temperature only, and in the case of ethylene oxide, a is proportional to the initial concentration, so that the half-life is independent of the initial concentration. This fact alone cannot be held to imply that the process is unimolecular. In the case of acetaldehyde n appears to reach a maximum value between 420° and 500°, where there are no data, and a increases more rapidly than the concentration, seeming to approach linearity at low temperatures.

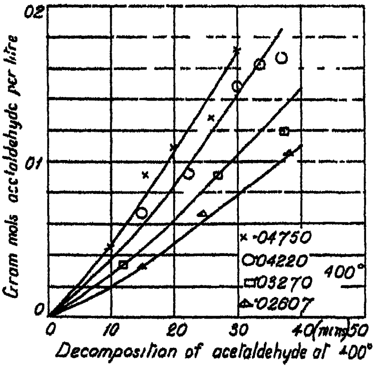

FIG. 6.

The graphs in Figs. 6 and 7 show the relationship between the observed and calculated data in the case of acetaldehyde and ethylene oxide.

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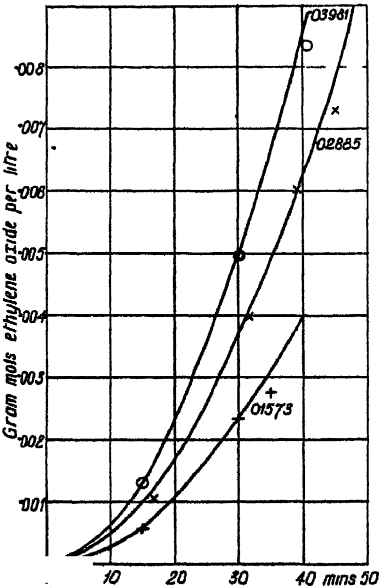
[7] Semenoff, *Chemical Kinetics and Chain Reactions*, 1935.

By plotting log $t_{\frac{1}{2}}$ for ethylene oxide against $1/T$, the value 44 K.cals has been obtained for E. In the case of acetaldehyde, the values for $t_{\frac{1}{2}}$ at initial concentration 0·02507 g.m.l. at temperatures between 420° and 360° give the value 40 K.cals. for E. The significance of these results is doubtful



Decomposition of ethylene oxide at 400°

FIG. 7.

In the case of methyl nitrite[*] the formula applies fairly well to the three points before the break point.

Now the rates of reaction (overall) in the cases of ethylene oxide and acetaldehyde are independent of the surface up to the break point, while the rate of formation of methane and condensate from pure ethane is materially dependent on the surface through the primary decomposition process. The formula (no. 23) applies most accurately to the result obtained (Table VI. A) with the empty thick-walled tube pretreated with hydrogen, a condition which seems to eliminate surface effects. Using the formula

$$x = 0{\cdot}003815\, t^{1{\cdot}195} \quad . \quad (24)$$

we obtain the results in Table IX.

(9) The Break in the x/t Graphs.

In the case of acetaldehyde, it has been shown that there is some probability that the limit of the break point is the half-life period, and that the period before the break point may be increased up to this limit by introducing hydrogen or methane, the effect of which is associated with some surface phenomena. There is no indication of chemical change. At 500° the half-life periods are practically coincident with the break points. The phenomena show certain similarities to such processes as the oxidation of methane, but considering the small energy change involved in the thermal decomposition of acetaldehyde, it seems dangerous to push the analogy too far.

(10) Phenomena Occurring at the Break Point.

From the study of the facts put forward in this paper, and in those which follow, it appears that the change represented by the breaks in the x/t-graphs may be due to phenomena occurring at the surface or in the gas phase. When it is clear that the change is associated with phenomena operating in the gas phase there is generally evidence that the slowing down of one process

TABLE IX.

Time.	½.	1.	2.	3.
(CH_4 + R) found	0·00167	0·00372	0·00907	0·01388
(CH_4 + R) calcd.	0·00167	0·00381	0·00874	0·01417

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[*] Carter and Travers, *Proc. Roy. Soc.*, *A*, 1937, 158, 495.

is always accompanied by the starting of another. The destruction of active centres of one kind is accompanied by the formation of active centres of another, the process being of the nature of an individual step in a chain process. This is probably what happens when the thermal decomposition of dimethyl ether is slowed down by the addition of nitric oxide.[9]

Interesting information may be gained from the study of the thermal decomposition of methyl nitrite.[8] This compound decomposes in the neighbourhood of 200° according to the equation,

$$2CH_3NO_2 = 2NO + CH_2O + CH_4O \quad . \quad . \quad . \quad (25)$$

but it is possible that the reaction also follows an alternative course represented by,

$$2CH_3NO_2 = N_2O + 2CH_2O + H_2O \quad . \quad . \quad . \quad (26)$$

The formation of NO is self-accelerated, and doubtless there is a background reaction, involving the formation of an isomeric body, the main process resulting from binary collision of the dissimilar molecules. At the same time a little carbon monoxide is formed, possibly by the reaction of formaldehyde with nitric oxide, this process being also self-accelerated. It is very noticeable that at the moment when the rate of formation of nitric oxide slows down, the concentration of the carbon monoxide begins to diminish, as it is probably oxidised to CO_2. Then, the rate of formation of both products again increases, till another break point is reached, when the phenomenon is repeated.

Now nitric oxide and carbon monoxide do not react at 200°, so that the nature of the chemical process involved is not clear. However, one must suppose that it is the active centres which give rise to the intermediate, and not the intermediate itself, or the NO, which is involved in this process, and that the break occurs when the concentration of the active centres reaches a certain maximum, at the moment when some other reactant, or reacting system, also reaches a certain concentration; the chain breaking process, so-called, then involves the initiation of another reaction.

In the case of ethane, and also of ethylene, there is a distinct drop in the hydrogen concentration at the break point, but the system is too complicated to determine the meaning of it.

In the case of acetaldehyde there is no sign of a chemical change intervening at the break point, the position of which appears to be determined by surface conditions, but to be limited to the half-life period. A similar phenomenon is associated with the oxidation of methane in the gas phase,[7] where the x/t-graph is represented by the formula No. 22. Another phenomenon must also be mentioned. Commonly, the break point is very sharp. Sometimes, however, the x/t-graph at the break seems to assume a sinuous form, the main reaction appearing *to run backwards* for a short interval. This is indicated in some of the experiments with acetaldehyde, and is very marked in the case of methyl amine. The phenomenon is being studied further.

(11) Thermal Change in Pure Ethylene.

With a view to testing the conclusions of Pease,[10] Hockin and I carried out some experiments on the condensation of pure ethylene, at 0·05 atoms

[9] Gay and Travers, *Nature*, 138, 546.

[10] Pease, *J. Am. Ch. Soc.*, 1931, 53, 613.

of carbon per litre initial concentration in silica apparatus at 360°. The results were very variable, and seemed to depend on surface conditions. The products were chain hydrocarbons with very little methane or hydrogen. Experiments were also carried out at 590°, but in this case the products were hydrogen, ethane, methane, and condensate consisting of aromatic hydrocarbons. The hydrogen appeared to be generated fast at first, and then more slowly, a sharp drop occurring at the break point. The rates of formation of ethane, methane, and condensate were self-accelerated a very sharp break point occurring in each case.

TABLE X.

Time, Minutes.	C_2H_4.	C_2H_6.	CH_4.	H_2.	R.	$\frac{P_{C_2H_4} \times P_{H_2}}{P_{C_2H_6}}$, atm.	$\frac{H}{C}$ in R.
	Gram Atoms per Litre.						
5	0·04107	0·00214	0·00056	0·00122	0·00550	0·066	1·45
10	0·02554	0·00718	0·00229	0·00164	0·01599	0·020	1·10
15	0·01598	0·00978	0·00420	0·00146	0·02004	0·0085	1·02
30	0·00948	0·01264	0·00531	0·00176	0·02257	0·0046	0·98
45	0·00652	0·01298	0·00630	0·00202	0·02420	0·0037	0·88

The rate of formation of methane and condensate is evidently small at first' so that they certainly are not formed directly from the ethylene alone. It seems probable that the whole process is initiated by the formation of acetylene and hydrogen, the former condensing, the latter reacting with ethylene yielding ethane, from which methane and condensate are produced, together with more hydrogen, by the process which we have discussed. The hydrogenation of the ethylene is the background reaction and as E is 11·5 K.cals. and as the reaction is exothermic to the extent of 30 K.cal., energy equivalent to 41·5 K.cals. must be disposed of in every primary act resulting in a hot ethane molecule. The acceleration of the process in which ethane molecules take part is therefore not surprising.

Assuming that the $(CH_4 + R)/t$ graphs can be represented by the equation No. 23, when a 0·0603 and $n = 1·4$, and differentiating, we can calculate the values of K_1 (equation no. 9) at 5 and 10 minutes. Using the data in Table X. graphically we can estimate the values of K_1 for 15-30 minutes and 30-45 minutes. We find (see Table XI.). The rate is 90 to 70 times greater than for bimolecular reaction before the break and still 5 times too great after the break, where, however, there is still a considerable departure from equilibrium conditions in the ethane-ethylene-hydrogen system.

TABLE XI.

Time.	Log K_1.
5 mins.	3·26
10 ,,	3·08
15-30 ,,	2·01
30-45 ,,	2·005

The results show that in such complex systems only very partial analysis is possible.

(12) Summary and Conclusions.

The result of the study of the thermal decomposition of simple organic compounds appears to support the view that the mechanism proposed in the first paragraph can be used explain the changes which take place. This, it must be observed, is based upon the assumption that the main reaction involves a simple bimolecular process, modified by the operation of what has been termed the ***background reaction.*** When the background reaction is eliminated, as in the case of ethane-ethylene-hydrogen equilibrium mixtures, the simple bimolecular character of the main reaction becomes perfectly clear.

This main, or rate determining reaction, leads to the formation of an *unstable intermediate,* which may yield one or more products, and it is the rate of formation of all the products together which measures the rate of the main process. These products are the result of a single activation process.

The overall rate of change, including,

(i) The background reaction,
(ii) The formation of the unstable intermediate,
(ii) The formation of the products from (ii)

can generally be represented by an equation,

$$x = at^n,$$

up to the break point, which is characteristic of the graphs representing the changes which we have considered, a being dependent on concentration and n on temperature. In some cases it is shown that a is proportional to the initial concentration, so that the half-life is independent on the initial concentration. However, it would be mistaking the formula for the fact to suggest that this is evidence that the process is unimolecular; indeed, the evidence is entirely in favour of the suggestion that the main process is bimolecular.

The nature of the phenomena occurring at the break point are considered. It is suggested that they may be due to changes in the gas phase, and in this case the slowing down of one process seems to involve the starting up of another. In other cases the break point seems to be associated with surface phenomena, and in these the limiting time at which the break occurs appears to be the half-life period, but no reason can be assigned for this fact.

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ON THE THERMAL DECOMPOSITION OF PROPANE, PROPYLENE, HYDROGEN EQUILIBRIUM MIXTURES.

BY MORRIS W. TRAVERS.

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In the previous paper, it was shown that the decomposition of simple organic compounds involved three stages, which were referred to as,

(1) The background reaction.
(2) The main reaction leading to the formation of an unstable intermediate.
(3) The decomposition of the intermediate with formation of one or more products.

In the case of ethane, the background reaction is the primary decomposition process. The final product is a mixture of methane and condensation products. In the case of pure ethane the rate of formation of methane and condensate, or the rate of disappearance of 2-carbon hydrocarbon, is represented by graphs curved towards the x-axis, and showing marked breaks. The causes of these phenomena are discussed and explained. When, however, the effect of the background reaction is eliminated, by experimenting with ethane-ethylene-hydrogen equilibrium mixtures instead of with pure ethane, at temperatures at which equilibrium in this system is rapidly established, it is found that the rate of reaction is represented by the simple bimolecular formula,

$$d(CH_4 + \text{Condensate})/dt = K(C_2H_4)(C_2H_6).$$

Previously Travers and Pearce[1] had put forward another explanation to account for the formation of methane and condensate from ethane and from the equilibrium mixtures, and when this work was completed I carried out series of experiments to see whether the same explanation applied to the case of propane-propylene-hydrogen equilibrium mixtures. It did not seem to apply. The experiments were carried out at 553°, because at that temperature the thermal reactions involving ethane and ethylene, which are products, are becoming relatively slow, while those involving propane and propylene are still relatively rapid. This was necessary to enable me to test the Travers-Pearce theory. Actually, to test the views which I now hold, this condition does not apply, for according to the present theory, starting from an equilibrium mixture of propane, propylene, and hydrogen, at a temperature at which the equilibrium reaction takes place fairly rapidly, the total amount of 3-carbon hydrocarbon transformed at any moment should be proportional to the product of the concentrations,

$$(C_3H_8)(C_3H_6).$$

It does not matter in the least whether the ethane or ethylene formed undergo subsequent change or not.

(2) Experimental Methods.

Propylene was made by decomposing isobutyl alcohol in contact with alumina, and propane by passing the propylene, together with excess of hydrogen, over asbestos coated with copper. The propane was treated with a little bromine water. Both gases were liquefied and fractionated.

The method of detailed analyses, described in previous papers, was used. The reaction tubes were of Pyrex glass, which is not recommended for such purposes; for, where surface reactions take place, the glass tends to change its properties gradually, and a drift in the results is observed.

After preliminary experiments, and using information derived from the experiments by Travers and Pearce, it was decided to experiment in the neighbourhood of 550°. At that temperature the rate of formation of condensate from the ethane and ethylene is relatively very slow, which was thought to be important in view of the ideas which were then held as to the mechanism which would operate in the decomposition of the propane and propylene. As a matter of fact, the interaction of the ethane and ethylene produced by the decomposition of the propane and propylene does not affect the latter process at all.

The general method of investigation was that used by Travers and Pearce.[1] However, in this case one has to deal with a mixture of propane, propylene, ethane, and ethylene in the fraction volatile at − 80°. The gas did not seem to contain more than traces of 4-carbon hydrocarbon, if any. The treatment of this fraction was as follows. It was divided into two parts, which were measured. One part was burned to CO_2 over hot copper, and from the result the C_3/C_2 ratio in the gas was determined. The second part was treated with a dilute solution of bromine in potassium bromide, introduced very slowly into the gas, so as to avoid replacement of hydrogen. The residue consisting of saturated hydrocarbons was measured and burned to CO_2 to determine the C_3/C_2 ratio. From these two results the quantities of C_3H_8, C_3H_6, C_2H_6, C_2H_4 could be calculated. This work required very accurate analyses.

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[1] *J. Soc. Chem. Ind.*, **53**, 321.

Several series of experiments were carried out with different reaction tubes, or with tubes which had been differently treated.

(3) The Experimental Results.

The value of the equilibrium constant $P_{C_3H_6}P_{H_2}/P_{C_3H_8} = k$, used in making up the equilibrium mixtures, was taken as approximately 0·08 (atm.) from the results of preliminary experiments. The mean value at 553° of the results of the experiments in Table I. is 0·085.

According to the theory put forward in the previous paper, effective collision of C_3H_8 and C_3H_6 molecules should result in the formation of an unstable complex (C_3H_8, C_3H_6), the rate of this process being determined by measuring the rate of increase in the sum of the products. This is a bimolecular process indicated by (2). Equilibrium in the system propane-propylene-hydrogen is in the meantime maintained by the background reaction (1). If this proceeds very rapidly the production of hot molecules in excess of the normal concentration tends to accelerate the main reaction. The nature of the processes in, and following the decomposition of the unstable intermediate, indicated by (3), are not for the moment important, as we only want to know the total amount of them, in terms of 3-carbon hydrocarbon disappearing from the system. However, it must be pointed out that the rapid change in the hydrogen concentration, associated with the conversion of the ethylene, which is first produced, into ethane, must be adjusted through the operation of the background reaction, and enhances the disturbance referred to. The process is therefore somewhat more complex than that involving 2-carbon hydrocarbons.

The three stages referred to in the first paragraph may now be represented by,

$$C_3H_8 = C_3H_6 + H_2 \quad . \quad . \quad . \quad . \quad (1)$$

$$C_3H_8 + C_3H_6 = (C_3H_8, C_3H_6) \quad . \quad . \quad . \quad (2)$$

$$(C_3H_8, C_3H_6) = S = CH_4 + C_2H_6 + C_2H_4 + \text{Condensate} \quad . \quad (3)$$

The decomposition of the unstable intermediate is represented by equation (3), but the relationships are not stoichiometric. The second and third processes are sensibly irreversible, and the second is the rate determining process. Then

$$dS/dt = K(C_3H_8), (C_3H_6)$$

In the calculations the unit in which the reactants and resultants are measured is gram atoms of carbon per litre. In order to calculate the value of K for time intervals $\Delta t = 0 - t_1$, $t_1 - t_2$, etc., the computation method described in the previous paper was used.

$$K = \Delta S/(\text{mean } C_3H_8)\ (\text{mean } C_3H_6)\Delta t.$$

This method makes the values of K seem more irregular than when successive values for $0 - t$ are calculated.

The mean value of log K (gram atom of carbon per litre) is 1·65, and, except in Series IV, the results do not depart very far from the mean. Taken with the experiments in the previous paper, they support the general theory which I have put forward to explain the mechanism of decomposition of a large group of simple organic compounds.

(4) The Decomposition of the Unstable Intermediate.

Study of the figures in Table I. suggests that methane and ethylene are probably the sole products of the primary decomposition of the intermediate (C_3H_8, C_3H_6). Ethane is a first secondary product, and, from

TABLE I.—THERMAL CHANGES IN PROPANE-PROPYLENE-HYDROGEN EQUILIBRIUM MIXTURES AT 553°

Gram Atoms of Carbon or Hydrogen per Litre.

Serial.	Ia.	Ib.	Ic.	Id.	IIa.	IIb.	IIIa.	IIIb.	IIIc.	IVa.	IVb.	Va.	Vb.	VIa.	VIb.
Time (hours)	0·5	1·125	2·25	3·0	0·75	1·50	0·5	1·0	1·665	1	2	0·5	1·067	0·55	1
Taken : H_2	0·01125	0·01125	0·01107	0·01103	0·01103	0·01115	0·00869	0·00872	0·00866	0·01128	0·01068	0·01115	0·01120	0·01121	0·01120
„ C_3H_8	0·04986	0·04986	0·04986	0·04986	0·04986	0·04986	0·04500	0·04500	0·04500	0·02390	0·02390	0·02493	0·02493	0·04980	0·04980
„ C_3H_6	0·01014	0·01014	0·01014	0·01014	0·01014	0·01014	0·01500	0·01500	0·01500	0·00610	0·00610	0·00507	0·00507	0·01014	0·01014
Found : H_2	0·01009	0·00877	0·00723	0·00567	0·00933	0·00508	0·00771	0·00668	0·00577	0·00976	0·00791	0·01039	0·00952	0·00986	0·00860
„ C_3H_8	0·04285	0·03431	0·01985	0·01652	0·03688	0·02628	0·03816	0·03187	0·02519	0·01996	0·01386	0·02150	0·01877	0·04079	0·03361
„ C_3H_6	0·00824	0·00680	0·00535	0·00701	0·01294	0·00913	0·01311	0·01120	0·00863	0·00355	0·00389	0·00533	0·00507	0·00910	0·01082
„ C_2H_6	0·00028	0·00283	0·00897	0·01076	0·00261	0·00629	0·00068	0·00284	0·00371	0·00054	0·00348	0·00063	0·00126	0·00201	0·00491
„ C_2H_4	0·00522	0·00661	0·00667	0·00431	0·00263	0·00450	0·00342	0·00313	0·00703	0·00294	0·00321	0·00112	0·00215	0·00622	0·00502
„ CH_4	0·00291	0·00623	0·01041	0·01228	0·00393	0·00896	0·00281	0·00542	0·00936	0·00206	0·00410	0·00120	0·00233	0·00310	0·00566
Condensate	0·00050	0·00322	0·00865	0·00911	0·00101	0·00484	0·00182	0·00544	0·00608	0·00095	0·00164	0·00022	0·00042	0·00216	0·00336
S	0·00891	0·01889	0·03480	0·03646	0·01018	0·02459	0·00873	0·01693	0·02618	0·00649	0·01243	0·00317	0·00616	0·01249	0·01895
k	0·066	0·059	0·066	0·085	0·110	0·059	0·090	0·095	0·105	0·056	0·076	0·090	0·087	0·073	0·091
Δt	0-05	05-1·125	1·125-2·25	2·25-3·0	0-0·75	0·75-1·5	0-0·5	0·5-1·0	1·0-1·667	0-1·0	1·0-2·0	0-0·5	0·5-1·067	0-0·55	0·55-1·0
log k	1·62	1·74	1·93	1·32	1·42	1·70	1·48	1·575	1·69	1·795	2·1	1·715	1·7	1·72	1·595

In Series VI., 0·00338 of ethylene was added initially, and this quantity must be subtracted in calculating S

the reaction of ethane and ethylene, condensate, and possibly more methane, result in the manner indicated in the previous paper. If this is the case the ratio,

$$(C_2H_6 + C_2H_4 + \text{Condensate})/CH_4$$

in gram atoms carbon per litre should be approximately equal to 2. That this is the case is shown by the figures for the initial periods taken from Table I.

TABLE II.

Series	I.	II.	III.	IV	V	VI.
$C_2H_6 + C_2H_4 +$ Condensate)	0·00600	0·00625	0·00593	0·00443	0·00297	0·00701
CH_4 . . .	0·00291	0·00393	0·00281	0·00200	0·00120	0·00310

The stoichiometric relationships are then represented by,

$$(C_3H_8, C_3H_6) + H_2 = 2C_2H_4 + 2CH_4$$

This suggests that the rupture in the complex takes place at a single bond, and that there is no need to assume that free radicals enter into the process.

In the case of the system ethane-ethylene it is not so easy to interpret the results. Referring to the previous paper it will be seen that for high hydrogen concentrations the only ultimate product is methane. As the hydrogen content of the equilibrium mixtures diminishes, the ratio,

(Carbon as Condensate)/(Carbon as Methane),

seems to approach unity. This suggests that from the complex, (C_2H_6, C_2H_4), under these limiting conditions, there is formed $2CH_4$ and a 2-carbon complex, which is of the nature of a radical. There seems to be evidence that neither ethylene nor ethane enter into the later stages of condensate formation; indeed to assume that such changes take place would be contrary to the principle which underlies the whole hypothesis.

(5) Conclusion.

From these results, taken with those contained in the previous paper, it seems clear that the main process which leads to the formation of the complex mixture of products which result from the thermal treatment of propane-propylene-hydrogen equilibrium mixtures, is a simple bimolecular reaction involving molecules of propane and propylene only. This reaction results in the formation of an unstable intermediate (C_3H_8, C_3H_6), from which the products themselves are derived.

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ON THE THERMAL DECOMPOSITION OF DIMETHYL ETHER.

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In the two previous papers it was shown that a number of simple organic substances behaved similarly. The process appears generally to proceed in three stages. The first, called the background reaction,

$$A \rightleftharpoons B(+ C) \quad . \quad . \quad . \quad . \quad (1)$$

is represented in the case of the simple hydrocarbons by the primary decomposition of a saturated hydrocarbon into an olefine and hydrogen, and in the case of acetaldehyde and other compounds by the formation of an isomer. The second stage involves bimolecular collision of the dissimilar molecules, one of which is a product of the background reaction, resulting in the formation of an unstable intermediate, thus

$$A + B = AB \quad . \quad . \quad . \quad . \quad (2)$$

This appears to be the rate-determining process, and it is self-accelerated owing to the increase in concentration of B as the reaction proceeds. There also appears to be superimposed on it a chain process originating in the background reaction. The third stage involves the decomposition of the unstable intermediate to yield single or *paired* products.

The behaviour of the alkyl ethers differs considerably from that of compounds of this class, and in the present paper we shall describe experiments which indicate the nature of the difference.

In the previous investigations on the thermal decomposition of dimethyl ether,[1] it has been assumed that the formation of methane, carbon monoxide and hydrogen takes place either by a single process, or by consecutive processes of the same order, represented by

$$(CH_3)_2O = CH_4 + CH_2O \quad . \quad . \quad . \quad (3)$$
$$CH_2O = CO + H_2 \quad . \quad . \quad . \quad . \quad (4)$$

and that the primary decomposition process can be followed by measuring the rate of increase in pressure at constant temperature and constant volume. In the experiments now described, the rate of formation of methane was measured by the method of detailed analysis. A measured quantity of dimethyl ether was condensed in a silica tube, which had been previously filled with hydrogen, heated to 600° overnight, and exhausted. The tube was then sealed, heated for a definite time at the reaction temperature, chilled, and the contents analysed. The details of the method have been described in several previous papers.

In the course of the investigation it was found that reactions other than those indicated by the two equations written above took place in the apparatus. One of the most important of these appeared to result in the formation of a hydrocarbon, probably mainly ethane, since the hydrogen concentration is always considerable, and a hydrocarbon condensate, probably formed from ethane and ethylene by the mechanism discussed in a previous paper.[2] An oxygen containing condensate, which was either methyl alcohol or a condensation product of formaldehyde, was also formed. The following equations represent some of the side reactions which may take place, and the order of their possible importance, that is, the extent to which they might be formed under equilibrium conditions is represented by the sign and magnitude of the free energy change (ΔF, American notation) in the process, calculated for 490° from the data compiled by Parkes and Huffman.[3]

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[1] Hinshelwood and Askey, *Proc. Roy. Soc., A*, 1927, 115, 215; Kassel, *J.A.C.S.*, 1932, 54, 3645; Steacie, *J. Physic. Chem.*, 1932, 36, 1562.

$$\left.\begin{array}{llll} CH_2O + H_2 & = CH_4O, & & \\ \Delta F = 14{\cdot}35; & k = 7{\cdot}4 \times 10^{-5} & & \end{array}\right\} \quad (5)$$

$$\left.\begin{array}{llll} (CH_3)_2O + H_2 & = CH_4O & + CH_4 & \\ \Delta F = -29{\cdot}9; & k = 5{\cdot}4 & & \end{array}\right\} \quad (6)$$

$$\left.\begin{array}{llll} 2CH_2O & = CH_4O & + CO & \\ \Delta F = -34{\cdot}47; & & & \end{array}\right\} \quad (7)$$

$$\left.\begin{array}{llll} (CH_3)_2O & = (CH_2)_2O & + H_2 & \\ \Delta F = \text{about } 17; & & & \end{array}\right\} \quad (8)$$

$$\left.\begin{array}{llll} (CH_3)_2O + H_2O & = 2CH_4O & & \\ \Delta F = 2{\cdot}8; & k = 0{\cdot}15 & & \end{array}\right\} \quad (9)$$

These figures give no indication of the rates of their reactions.

The reactions represented by (5), (8) and (9) need not be considered. Equations (6) and (7) might reasonably be supposed to yield methane and carbon monoxide; and reference to Table XII. will show that addition of hydrogen to the dimethyl ether will, in some cases, increase the difference $CH_4 - H_2$. However, the irregularity of the result, and the relatively small influence of the concentration of the hydrogen indicates that the effect on the primary decomposition of dimethyl ether is probably negligible. Fletcher[4] suggested that methyl alcohol is formed through reaction (7), and this may account for the slight excess of hydrogen over carbon monoxide in some experiments. Reaction (9) can only take place if water is formed in the process which leads to the formation of hydrocarbon, the mechanism of which is unknown. It is not likely to be of material importance.

In order to obtain some idea of the nature of the by-products in the thermal decomposition process, two experiments were carried out at 490°, at concentrations corresponding to 0·04 gram mols. per litre. The reaction tubes were heated for fifteen and for forty-five minutes respectively, when the amount of decomposition corresponded to 48 and 92 per cent. of the dimethyl ether. While the tubes were cooled to − 180°, methane, hydrogen, and carbon monoxide were pumped off. At − 80° gas was pumped off containing dimethyl ether, carbon dioxide, and the hydrocarbon. From the latter fraction the dimethyl ether was absorbed with strong sulphuric acid, the carbon dioxide was absorbed by potash. While it was still at − 80° the reaction tube was sealed to a silica stem, oxygen was introduced, the tube again sealed, heated, and the contents analysed.

Table I. shows the results of the analyses :—

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[2] *This Journal*, p. 733.
[3] *Free Energies of Some Organic Compounds*, 1932.
[4] *Proc. Roy. Soc., A*, 1934, 146, 357.

TABLE I.

	I			II.		
	C.	H.	O.	C.	H.	O.
$(CH_3)_2O$ . . .	0·08000	0·24000	0·04000	0·08000	0·24000	0·04000
H_2		0·02470			0·06180	
CO	0·01381	--	0·01381	0·03454		0·03454
CH_4 . . .	0·01813	0·07252	- -	0·03525	0·14100	—
$(CH_3)_2O$ . . .	0·04156	0·12468	0·02078	0·00643	0·02529	0·00321
CO_2 . . .	0·00039	--	0·00078	0·00027		0·00054
C_2H_4 . . .	0·00026	0·00078	—	0·00022	0·00066	—
Non-volatile at —80°	0·00570	0·01156	—	0·00332	0·00904	—
Unaccounted for .	0·00015	0·00570	0·00463	0·00003	0·00221	0·00171

Now, if the decomposition process had followed its normal course, indicated by equations (1) and (2), the quantity of methane produced should equal the quantity of dimethyl ether decomposed, instead of the quantity found (Table II.). Also, the hydrogen and carbon monoxide should be produced in equal quantities, instead of those found (Table III.).

TABLE II.

(*Gram mols. per litre.*)

		II.
Methane .	0·01813	0·03525
Dimethyl ether decomposed	0·01922	0·03678
Difference	0·00109	0·00153

Finally, the carbon, hydrogen, and oxygen remaining in the residue should have the atomic ratio corresponding to CH_2O, instead of showing a large excess of hydrogen. The residue must consist of hydrocarbon condensate, possibly with some methyl alcohol and traces of water. Since the C/H ratio in the residue from the fifteen-minute experiment is nearly $\frac{1}{2}$, it is probable that it consists of condensed formaldehyde with some hydrocarbon, the latter reckoned as $(CH_2)_n$, being about 20 per cent. of the whole. At this stage little methyl alcohol seems to be formed.

It seems probable that the rate of the primary decomposition process may be measured with reasonable accuracy during the early stages of the reaction by observing the rate of formation of methane. However, it is of no use attempting to follow the process to anywhere near complete decomposition. The experiments also indicate that pressure measurement is not a reliable method of following the decomposition process.

TABLE III.

(*Gram mols. per litre.*)

		II.
Carbon monoxide	0·01381	0·03454
Hydrogen . .	0·01238	0·03093
Difference .	0·00142	0·00361

The whole of the phenomena associated with the decomposition of dimethyl ether differ from those associated with the group of compounds which includes ethane-ethylene, acetaldehyde, ethylene oxide, acetone, methylamine, and methyl nitrite, which have been shown in a previous paper [2] to behave very similarly. In the first place, the effect of the surface is very marked, so much so that it has been found very difficult to obtain concordant results, even with a single reaction tube treated in exactly the same manner before each experiment. The graphs representing the rates of formation at constant temperature, with a particular reaction tube, are linear, or slightly flexed towards the time axis. The initial angles which these graphs make with the time axis vary enormously with different tubes, but the incidence of the break for the same temperature and initial conditions, is always at the same time from the start. The incidence of the break is clearly not a surface effect. The time at which it appears increases with rise of temperature or decrease in concentration, and *vice versa* (Table IV.).

TABLE IV.—INCIDENCE OF BREAK POINT (Minutes)

Initial $(CH_3)_2O$ gm. mols. litre.	0·02	0·01	0·005
470°	20	33	50
490°	40	63	66

At lower and higher temperatures respectively, the break occurs soon after the reaction starts, or when it is nearly complete.

In Table V. we have set down the results of four sets of experiments as below :—

1. Tube D, 34·4 c.c., a new tube.
2. Tube A, 38·5 c.c., used for two earlier series.
3. Tube E′, 23·0 c.c., packed with rods, previously used for experiments with ethylene oxide. Volume empty, 37·7 c.c.
4. Tube E″, as above, but for unknown reason it had changed its character.

TABLE V.

Temp 490°. *Initial* $(CH_3)_2O$ 0·01 *gm. mols. litre. Time minutes.*

1. *Tube D* (*Break at* 65 *min*).

t	15	30	45	60	70	90	110
CH_4	0·00243	0·00421	0·00595	0·00735	0·00799	0·00873	0·00907
H_2	0·00129	0 00293	0·00472	0·00631	0·00711	0·00776	0·00814
CO	0·00127	0·00308	0·00488	0·00640	0·00701	0·00794	0·00847

2. *Tube A* (*Break at* 65 *min.*).

t	20	40	60	80	100
CH_4	0·00257	0·00456	0·00632	0·00729	0·00806
H_2	0·00141	0·00321	0·00505	0·00604	0·00680
CO	0·00138	0·00327	0·00519	0·00614	0·00707

3. *Tube E′* (*Break at* 65 *min.*).

t	30	60	75	92	100	120	150
CH_4	0·00161	0·00321	0·00370	0·00376	0·00387	0·00490	0·00559
H_2	0·0058	0·00188	0·00243	0·00225	0·00246	0·00322	0 00396
CO	0·0071	0·00203	0·00253	0·00222	0·00250	0·00345	0·00448

4. *Tube E″* (*Break at* 60-70 *min.*).

t	45	71	92	120	165
CH_4	0·00193	0·00300	0·00327	0·00293	0·00485
H_2	0·0095	0·00133	0·00180	0·00165	0·00277
CO	0·00102	0·00162	0·00186	0·00180	0·00321

That the process is self-accelerated, but to a different degree in the different tubes, is shown from the values of

$$dCH_4/dt/(CH_3)_2O,$$

where $(CH_3)_2O$ is the concentration of dimethyl ether after a time interval t, which are given in Table VI. The results relate to observations before the break-point. After the break-point, both the rate of formation of methane, and the rate of formation of hydrogen and of carbon monoxide slows down.

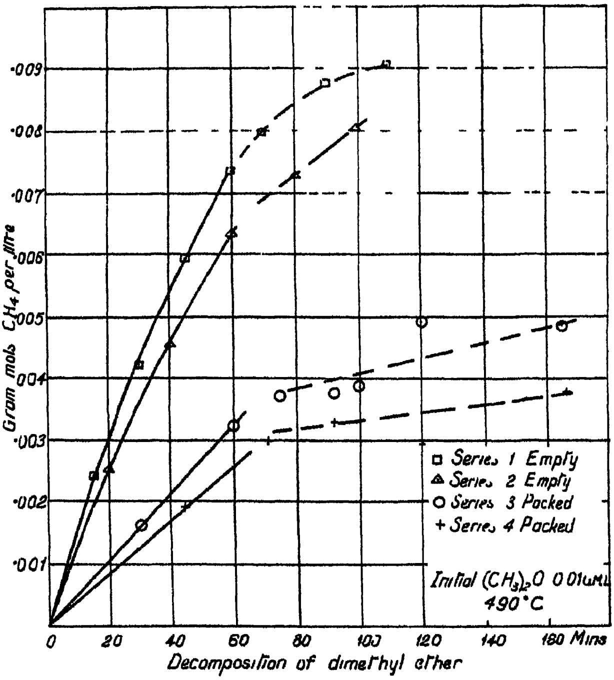

FIG. 1.

The effect of packing the tube in reducing the rate of reaction, and also the acceleration, seems to be considerable, but the effect seems to be due rather to increase in the effective surface than the reduction of the effective diameter. Packing has no apparent effect on the incidence of the break-point.

TABLE VI.

Time (minutes).	10	25	35	45	55
Series 1 Empty . .	0·178	0·201	0·218	0·248	0·296
,, 2 ,, . .	0·145	0·158	0·169	0·183	0·190
,, 3 Packed . .	0·0565	0·062	0·066	0·070	0·076
,, 4 ,, . .	0·044	0·047	0·049	0·052	0·054

Table VII. contains smoothed data obtained in a large number of series of experiments.

TABLE VII.

(1) 530°. *Tube A.* 0·01 *g.m l.*

t	5	10	15	20	25
CH_4	0·00239	0·00438	0·00614	0·00756	0·00883

(2) 530°. *Tube D.* 0·01 *g.m.l.*

t	5	10	15	20	25
CH_4	0·00228	0·00421	0·00590	0·00735	0·00862

(3) 520°. *Tube C.* 0·0025 *g.m.l.*

t	10	20	30	40	50	60
CH_4	0·00044	0·00083	0·00119	0·00149	0·00176	0·00200

TABLE VII —*Continued*,

(4) 520°. *Tube B.* 0·005 *g m.l.*

t	10	15	20	25	30
CH_4	0·00150	0·00219	0·00286	0·00348	0·00402

(5) 520 . *Tube C.* 0·005 *g m l*

t	10	15	20	25	30	35
CH_4	0·00158	0·00248	0·00309	0·00373	0·00427	0·00464

(6) 520°. *Tube B.* 0·02 *g.m.l.*

t	10	12·5	15	17·5	20	22·5
CH_4	0·00910	0·01110	0·01300	0·01480	0·01650	0·01810

(7) 520°. *Tube C.* 0·02 *g.m.l.*

t	10	12·5	15	17·5	20	22·5
CH_4	0·01030	0·01250	0·01460	0·01680	0·01840	0·02010

(8) 510° *Tube D.* 0·005 *g.m.l.*

t	15	20	25	30	35	40	45
CH_4	0·00137	0·00178	0·00219	0·00257	0·00293	0·00326	0·00359

(9) 510°. *Tube A.* 0·005 *g.m.l.*

t	10	20	30	40	50
CH_4	0·00093	0·00184	0·00258	0·00326	0·00388

(10) 510°. *Tube A.* 0·01 *g.m.l.*

t	10	15	20	25	30	35	40
CH_4	0·00232	0·00339	0·00438	0·00530	0·00613	0·00691	0·00761

(11) 510°. *Tube D.* 0·01 *g.m.l.*

t	10	15	20	25	30	35	40
CH_4	0·00230	0·00336	0·00432	0·00520	0·00602	0·00679	0·00748

(12) 510°. *Tube A.* 0·02 *g.m.l.*

t	10	15	20	25	30	35	40
CH_4	0·00664	0·00932	0·01158	0·01352	0·01524	0·01672	0·01806

(13) 510°. *Tube D.* 0·02 *g.m.l.*

t	15	20	25	30	35	40
CH_4	0·00892	0·01126	0·01324	0·01504	0·01676	0·01850

(14) 490°. *Tube C.* 0·005 *g.m.l.*

t	20	30	40	50	60	70	80
CH_4	0·00130	0·00187	0·00237	0·00283	0·00323	0·00360	0·00394
t						100	120
CH_4						0·00426	0·00442

(15) 490°. *Tube D.* 0·005 *g.m.l.*

t	30	40	50	60	70
CH_4	0·00142	0·00188	0·00230	0·00272	0·00308

(16) 490°. *Tube A.* 0·01 *g.m.l.*

t	20	30	40	50	60	80	100
CH_4	0·00254	0·00363	0·00462	0·00554	0·00633	0·00727	0·00805

(17) 490°. *Tube D.* 0·01 *g.m.l.*

t	20	30	40	50	60	70	80
CH_4	0·00303	0·00430	0·00542	0·00643	0·00735	0·00799	0·00843
t					90	100	110
CH_4					0·00875	0·00896	0·00905

TABLE VII—*Continued*

(18) 490°. *Tube A.* 0·02 *gm/l.*

t	15	20	25	30	35	40
CH_4	0·00520	0·00672	0·00811	0·00950	0·01082	0·01202

(19) 470°. *Tube C.* 0·005 *gm/l.*

t	80	100	120	140	160	180
CH_4	0·00123	0·00141	0·00158	0·00174	0·00191	0·00208

(20) 470°. *Tube A.* 0·01 *gm/l.*

t	60	90	120	150	180	210	240
CH_4	0·00289	0·00382	0·00468	0·00545	0·00611	0·00671	0·00723

(21) 470°. *Tube B.* 0·02 *gm/l.*

t	20	30	40	50	60	70	80
CH_4	0·00450	0·00638	0·00800	0·00940	0·01080	0·01206	0·01328
t						90	120
CH_4						0·01442	0·01748

Treatment of the Experimental Results.

We have used a method of analysing the results which is at least plausible, though we shall criticise it later. We calculate from the data in Table VII. the values of $d(CH_4)/dt$, and plot the logarithms against the time, obtaining graphs which are linear, or nearly so. The intercepts on the log $d(CH_4)/dt$ axis are the logarithms of the initial velocities. These values, and the logarithms of the initial concentrations for series of experiments with the same tube, are set down in Table VIII.

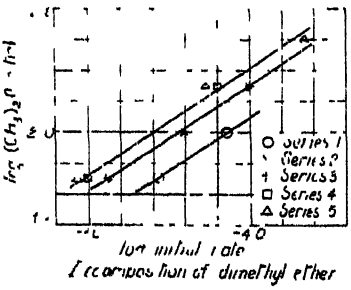

FIG. 2.

The values of log $(CH_3)_2O$ (initial) are plotted against log $d(CH_4)/dt$ (initial), and from the graphs, Fig. 2, we find the empirical relationship.

$$(\text{Initial rate}) \propto (\text{Initial concentration})^{1·6} \quad . \quad . \quad (10)$$

TABLE VIII.

Serial.	Temp.	Tube.	Log $(CH_3)_2O$ Initial.	Log (dCH_4/dt) Initial.
(1)	490°	A	— 1·699	— 3·432
		A	— 2·000	— 3·857
(2)	510°	A	— 1·699	— 3·114
		A	— 2·000	— 3·590
		A	— 2·301	— 4·009
(3)	510°	D	— 1·699	— 3·135
		D	— 2·000	— 3·599
		D	— 2·301	— 4·009
(4)	520°	B	— 1·699	— 2·997
		B	— 2·301	— 3·801
(5)	520°	C	— 1·699	— 2·938
		C	— 2·301	— 3·735
		C	— 2·602	— 4·338

The rates after the break-point are difficult to determine, as the experimental results tend to become erratic, probably for the reason that the reaction is slowed down by the phenomena operating at the surface and in the gas phase, the effects of which are superimposed. It might be possible to investigate the slower rate of reaction by means of experiments at temperatures below 470°, but as the phenomena must be more complex than those at the higher temperatures, it is doubtful if it would be worth while.

The Effect of Temperature.

The effect of temperature has been determined by application of the same method, and in Table IX. the data are arranged so as to enable us to compare the rates obtained from series of experiments with the same tube and at the same initial concentration but at different temperatures.

TABLE IX

Serial.	Concentration.	Tube.	Temperature	Log Initial Rate.	$\frac{1}{T} \times 10^3$.	E, (K cals.).
(1)	0·02	A	510°	− 3·114	1·277	42
		A	490°	− 3·432	1·311	
(2)	0·01	A	530°	− 3·292	1·245	40
		A	510°	− 3·599	1·277	
		A	490°	− 3·857	1·311	
(3)	0·01	D	530°	− 3·312	1·245	40
		D	510°	− 3·599	1·277	
(4)	0·005	D	510°	− 4·009	1·277	39·5
		D	490°	− 4·292	1·311	
(5)	0·005	B	520°	− 3·801	1·261	38
		B	490°	− 4·215	1·311	
(6)	0·005	C	520°	− 3·735	1·261	37·5
		C	490°	− 4·143	1·311	

The value of E falls slightly with initial concentration, reaching a lower limit at 38 K.cals. The result differs very considerably from that obtained by Hinshelwood and Askey, namely, 58 K.cals. However, they were measuring the rate of two superimposed processes having different characteristics, which may account for the difference.

The Thermal Decomposition of the Secondary Formaldehyde.

Fletcher [4] investigated the thermal decomposition of formaldehyde by measuring the increase in pressure at constant volume. He found that condensation took place to a small extent initially, the condensation product itself decomposing at later stages, so that the process was represented very closely by equation (4), the reaction being bimolecular. The value of E from the temperature coefficient was found to be 44·5 K.cals, and using this value to calculate the value of the velocity constant, agreement with the observed value was very close indeed. Since, apart from side reactions, which operate to a very small extent, the decomposition process can follow no other course to that indicated by equation (4), this result is to be expected.

In the present case, formaldehyde is a product of the reaction represented by equation (3), which may be regarded as a background reaction, in the sense in which the term has been used in connection with the thermal decomposition of simple organic compounds, but in this case it is not a reversible process. The concentration of the reactant is zero at zero time, and the molecules carry a share of the energy of activation, less the energy required for the decomposition process, which is, in this case, a very small quantity. The probability of reaction is therefore greater than in the case of the primary decomposition of formaldehyde. From analogy with other cases of the decomposition of simple organic compounds, the amount of formaldehyde, x, decomposed in time t should be given by,

$$x = at^n \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

TABLE X.—EXPERIMENTS WITH TUBE A.

No. 1. (530°. 0·01 g.m.l. *a* = 0·000225, *n* = 1·124, $t_{\frac{1}{2}}$ = 15·75.)

t	5	10	15	20	25·5
H_2	0·00048	0·00297,	0·00477	0·00651₅	0·00860,
CO	0·00049	0·00304	0·00476	0·00654	0·00861
Graph	0·00138	0·00302	0·00477	0·00655	0·00865

No. 12. (510°. 0·02 g.m.l. *a* = 0·000300, *n* = 1·063, $t_{\frac{1}{2}}$ = 22·3.)

t	10	20	30	40
H_2	0·00342	0·00897	0·01336	0·01558
CO	0·00343	0·00927	0·01307	0·01625
Graph	0·00427	0·00892	0·01305	0·01865

No. 10. 510°. 0·01 g.m.l. *a* = 0·000130, *n* = 1·063, $t_{\frac{1}{2}}$ = 30·9.)

t	10	20	30	40
H_2	0·00108	0·00321	0·00467	0·00653
CO	0·00102	0·00313	0·00479	0·00653
Graph	0·00151	0·00315	0·00468	0·00653

No 9. (510°. 0·005 g.m.l. *a* = 0·000055, *n* = 1·060, $t_{\frac{1}{2}}$ = 36·2.)

t	10	20·5	30	40
H_2	0·00036	0·00130	0·00216	0·00273
CO	0·00029	0·00103	0·00217	0·00267
Graph	0·00064	0·00139	0·00209	0·00285

No. 16. (490°. 0·02 g.m.l. *a* = 0·000246, *n* = 0·964, $t_{\frac{1}{2}}$ = 40·7.)

t	20	30	40	60
H_2	0·00403	0·00691	0·00975	0·01459
CO	0·00418	0·00737	0·01038	--
Graph	0·00483	0·00723	0·00975	0·01440

The amounts of hydrogen and carbon monoxide formed together with the methane were determined in every experiment, and the complete data are given in the case of the experiments recorded in Table V. A further set of data for experiments with the tube A is set down in Table X., and these data have been used to test the suggestion put forward above. This is the most complete series of experiments with a single reaction tube which are available, and can be treated in this way, but unfortunately the experimental results with this tube, at 490° and at 0·01 g.m.l. are not sufficiently regular to be useful. The values of *x* obtained by plotting the logarithms of the hydrogen and of the carbon

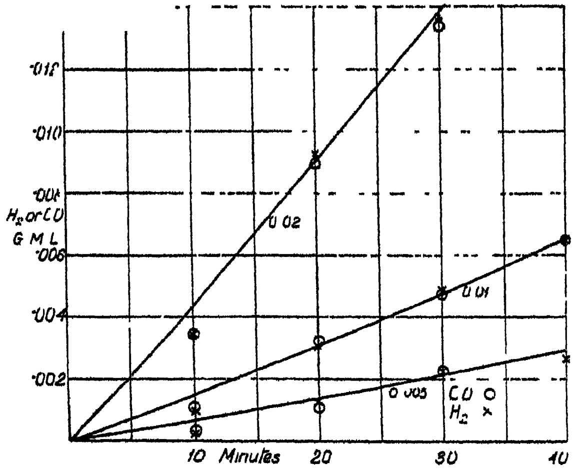

FIG. 3.—Decomposition of secondary formaldehyde at 510°.

monoxide formed in time *t* against log *t*, and drawing straight lines through the points are set down in the table. The results of the experiments at 510° are plotted in Fig. 3.

The observed points for the shortest time intervals always lie below the graphs (Fig. 3), and, as in the experiments of Fletcher, this is possibly caused by the formation of condensation products at the surface. The values of $t_{\frac{1}{2}}$ vary inversely as the initial concentration, but the values have no direct significance, and the values of *E* calculated from the values of $t_{\frac{1}{2}}$ in the pairs of experiments nos. 1 and 10, nos. 12 and 9, namely, 41 and 36 K.cals., are probably determined by the temperature coefficient of the primary decomposition process.

The Effect of Adding Hydrogen, Methane, and Carbon Monoxide.

In these experiments dimethyl ether at 0·01 g.m.l. initial concentration was heated for thirty minutes at 490°, first alone, and then with increasing quantities of hydrogen, methane, or carbon monoxide. The results are set down in Tables XI., XII., and XIII.

The effect of methane (Table X.) is to increase the rate of the primary, and consequently of the second reaction. The effect is relatively small, and apparently linear with the methane concentration. Only the addition

TABLE XI.—INFLUENCE OF METHANE.

Mean CH_4.	CH_4.	H_2.	CO.
	I. *Tube B.*		
0·00163 *	0·00326	0·00198	0·00203
0·00866	0·00352	0·00253	0·00256
0·01529	0·00385	0·00278	0·00287
	II. *Tube C.*		
0·00169 *	0·00338	0·00213	0·00222
0·00896	0·00374	0·00273	0·00284
0·01637	0·00398	0·00295	0·00299
0·02268	0·00414	0·00334	0·00329

* No CH_4 added.

TABLE XII.—INFLUENCE OF HYDROGEN.

Mean H_2.	CH_4.	H_2.	CO.	CO − H_2.
		I. *Tube B.*		
0·00142 *	0·00414	0·00285	0·00302	0·00017
0·00900	0·00540	0·00383	0·00409	0·00026
0·01605	0·00649	0·00523	0·00537	0·00014
0·02928	0·00728	0·00570	—	—
0·03660	0·00743	0·00580	0·00622	0·00042
0·05105	0·00780	0·00617	0·00671	0·00054
		II. *Tube C. first experiment.*		
0·00140 *	0·00420	0·00281	0·00302	0·00021
0·00684	0·00518	0·00373	0·00385	0·00012
0·01554	0·00583	0·00426	0·00450	0·00024
0·02342	0·00634	0·00507	0·00483	—
0·02839	0·00657	0·00507	0·00535	0·00035
		III. *Tube C, after experiment with* CO.		
0·00057 *	0·00233	0·00103	0·00117	0·00014
0·00848	0·00316	0·00172	0·00182	0·00010
0·01229	0·00384	0·00204	0·00256	0·00052
0·01565	0·00437	0·00221	0·00298	0·00076
0·02141	0·00472	0·00199	0·00328	0·00129

* No H_2 added.

of very large quantities of hydrogen would yield results which could be analysed.

The effect of adding hydrogen is shown by the results in Table XII. Those of Series I. and II. are plotted in Fig. 4. Neglecting the effect of side reactions and assuming that the quantity of dimethyl ether can be obtained by difference, the relationship between the amount of dimethyl ether disappearing in each experiment, and the mean hydrogen concentration is given by,

$$-d[(CH_3)_2O]/d(H_2) = K[(CH_3)_2O]/[H_2]_1, \quad . \quad . \quad (12)$$

$$\log \frac{[(CH_3)_2O]_2}{[(CH_3)_2O]_1} = K \log \frac{[H_2]_1}{[H_2]_2} \quad . \quad . \quad . \quad (13)$$

Taking the smoothed data from the graphs we have for Series I. and II. :—

TABLE XIII.

Series I.

H_2	0·01		0·02		0·03		0·04		0·05
$\log \frac{[H_2]_2}{[H_2]_1}$		0·301		0·176		0·125		0·097	
$(CH_3)_2O$	0·00432		0·00328		0·00272		0·00240		0·00220
$\log \frac{[(CH_3)_2O]_1}{[(CH_3)_2O]_2}$		0·1296		0·0813		0·0544		0·0378	
$1/K$		0·43		0·46		0·43		0·40	

Series II.

H_2	0·005		0·01		0·015		0·02		0·025
$\log \frac{[H_2]_2}{[H_2]_1}$		0·301		0·176		0·125		0·095	
$(CH_3)_2O$	0·0052		0·0046		0·00415		0·00385		0·0036
$\log \frac{[(CH_3)_2O]_1}{[(CH_3)_2O]_2}$		0·083		0·045		0·036		0·026	
$1/K$		0·27		0·255		0·29		0·265	

Series III.

H_2	0·0057		0·00848		0·01229		0·01567		0·02143
$\log \frac{[H_2]_2}{[H_2]_1}$		0·172		0·1615		0·115		0·1365	
$(CH_3)_2O$	0·00767		0·00684		0·00616		0·00563		0·00528
$\log \frac{[(CH_3)_2O]_1}{[(CH_3)_2O]_2}$		0·0497		0·0455		0·0391		0·0379	
$1/K$		0·285		0·28		0·35		0·275	

The influence of the hydrogen is different in the case of the two tubes. The third series of experiments was carried out with the tube C after it had been used for the experiments with carbon monoxide. It had changed its character, giving a very much lower rate of decomposition of dimethyl ether. The value of *K* calculated from the actual data, which are a little irregular, is found (Table XIII.) to be unchanged. This would point to the conclusion that there are two phenomena controlling the rate of decomposition of the dimethyl

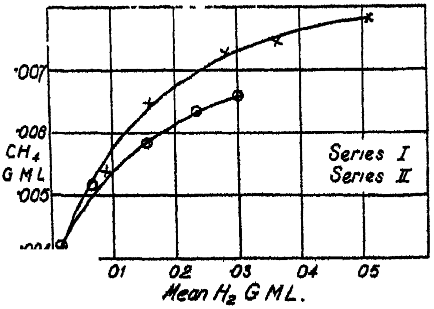

FIG. 4.

ether, both of them dependent on surface activity, but only one of them influenced by hydrogen concentration.

There is at the same time some reaction involving disappearance of hydrogen as is shown by the increase in the difference ($CO - H_2$) with increase in hydrogen concentration.

The effect of adding carbon monoxide is shown by the results in Table XIV. It is similar to that of hydrogen but more complex. The graph obtained by plotting the sums of the mean concentrations of carbon monoxide and hydrogen † against the methane formed shows two very marked maxima. The difference $H_2 - CO$ also increases to a maximum. The experiment was repeated with another tube, but in this case the influence of the carbon monoxide on the quantity of dimethyl ether decomposed was very small, as was the difference $H_2 - CO$.

TABLE XIV. INFLUENCE OF CARBON MONOXIDE.

Mean CO.	CH_4.	H_2	CO.	$H_2 - CO$.	Mean ($CO+H_2$).
			Tube C.		
0·00075 *	0·00255	0·00144	0·00150	— 0·00006	0·00147
0·00966	0·00306	0·00203	0·00177	— 0·0026	0·01067
0·01444	0·00261	0·00155	0·00121	— 0·00034	0·01521
0·01821	0·00297	0·00159	0·00108	— 0·00051	0·01901
0·01936	0·00361	0·00241	0·00162	— 0·00081	0·02056
0·02168	0·00430	0·00298	0·00168	— 0·00130	0·02317
0·02224	0·00257	0·00284	0·0060	— 0·00220	0·02306
0·02583	0 00302	0·00202	0·00122	— 0·00080	0·02684

* No CO added.

The Effect of Nitric Oxide.

While this work was in progress Staveley and Hinshelwood [5] published an account of their experiments on the effect of nitric oxide on the rate of decomposition of diethyl ether. As it seemed worth while examining the parallel case of dimethyl ether, and testing their conclusions by our own methods, we carried out the following experiments.

TABLE XV.—NITRIC OXIDE AND DIMETHYL ETHER.

Series I.

520°. *Initial* $(CH_3)_2O$ = 0·00458 g.m.l. *Time* 15 *minutes.*

Serial.	Initial NO.	Final NO.	H_2.	CO.	CH_4.	CO.	Final $(CH_3)_2O$.
1	0·00000	0·00000	0·00203	0·00216$_5$	0·00250	0·00006$_5$	0·00233
2	0·00005$_5$	—	—	0·00011	0·00014	0·00004$_5$	0·00442$_5$
3	0·00015	—	—	0·00003$_5$	0·00015	0·00001$_5$	0·00441
4	0·00026	0·00011	0·00003$_5$	0·00005	0·00014	0·00005	0·00451
5	0·00074$_5$	0·00061	—	0·00012	0·00027	0·00002$_5$	—
6	0·00161	0·00134$_5$	—	0·00016	0·00036	0·00007$_5$	0·00414
7	0·00526$_5$	0·00444$_5$	—	0·00100	0·00106$_5$	0·00016	0·00345
8	0·01366	0·01026	—	0·00260	0·00200	0·00038	0·00202$_5$
9	0·02931	0·02126	0·00020	0·00377	0·00231	0·00076	0·00094$_5$

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† The latter being much more active than the other gases.

[5] *Proc. Roy. Soc., A*, 1936, 154, 335.

The measured quantity of dimethyl ether was condensed in the reaction tube, cooled in liquid oxygen, and then a measured quantity of nitric oxide was added, and the tube sealed. The nitric oxide remaining uncondensed in the apparatus was then measured. After heating and chilling the tube, the nitric oxide was collected with the fraction volatile at 180°; but it was necessary to collect the fraction volatile at 80 , and condense and evaporate it repeatedly at 180° to remove from it all traces of nitric oxide.

The nitric oxide was absorbed from the more volatile fraction by means of a solution obtained by treating a solution of chromic chloride with metallic zinc. The nitric oxide is absorbed completely and irreversibly.[6]

The first series of experiments was carried out by successively increasing quantities of nitric oxide to a fixed quantity of dimethyl ether, and heating for fifteen minutes.

The thermal decomposition process in the case of diethyl ether is much more complex than in the case of dimethyl ether on account of the reactivity of the ethylene which is formed, which makes it difficult to obtain exact analytical results in that case. Our results do not therefore agree exactly with those of the other observers. As we have already pointed out[7] it is noticeable that we are dealing with at least two distinct processes. The one is the normal decomposition of dimethyl ether, which is completely suppressed by the addition of a very small quantity of nitric oxide. The other is a process involving the oxidation of dimethyl ether, which is strongly self-accelerated, and is possibly of the acetaldehyde type. The data obtained in other series of experiments are set down in Table XVI. In these

TABLE XVI.—NITRIC OXIDE AND DIMETHYL ETHER.

Time.	Initial NO.	Final NO.		CO.	CH_4.	CO_2.
			Series IIa (No. NO).			
10	0·00000	0·00000	0·00101$_5$	0·00120	0·00163	—
15	0·00000	0·00000	0·00203	0·00216$_5$	0·00249	0·00006$_5$
25	0·00000	0·00000	0·00284	0·00319	0·00383	-
			Series IIb.			
10	0·00074	·	—	0·00006$_5$	0·00017	
20	0·00070	0·00056	—	0·00017$_5$	0·00037$_5$	0·00005
25	0·00070	0·00050		0·00019	0·00042	0·00013
27-25	0·00070	0·00052		0·00023		0·00010$_5$
30	0·00073	0·00045	0·00004	0·00027	0·00040	0·00004
32-25	0·00075$_5$	0·00040	0·00005	0·00024$_5$	0·00052$_5$	0·00015
35	0·00073	0·00043	0·00004$_5$	0·00026$_5$	0·00059	0·00012
50	0·00073$_5$	0·00026	0·00009	0·00047	0·00075$_5$	0·00014
70	0·00075	0·00009	0·00016	0·00056	0·00105$_5$	0·00024
			Series IIc.			
15	0·00161	0·00134	—	0·00016	0·00036	0·00007$_5$
20-25	0·00162	0·00126	0·00005	0·00023$_5$	0·00054$_5$	0·00010$_5$
30	0·00161$_5$	0·00101	0 00002	0·00050$_5$	0·00088$_5$	0·00016$_5$
35	0·00162	0·0090	0·00003	0·00062$_5$	0·00105	0·00019$_5$
40	0·00160$_5$	0·0090	0·00005$_5$	0·00063$_5$	0·00107	0·00023
			Series IId.			
7·5	0·01362	0·01222	0·00014	0·00065	0·00083$_5$	0·00013
15	0·01366	0·01026	—	0·00260	0·00200	0·00038
15·5	0·01365	0·01004	0·00004	0·00244	0·00200	0·00045$_5$
25	0·01367	0·00857	0·00029	0·00300	0·00264	0·00061

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[6] Chesneau, *C. r.* 1899, 129, 100.

[7] *Nature*, 138, 576.

experiments mixtures of dimethyl ether and nitric oxide of constant composition were heated for increasing time intervals, and the products of reaction were determined. We have not been able to arrive at any conclusions as to the course of the reaction. However it is noticeable that the hydrogen content of the product is always small, that nitric oxide disappears from the gas, and that the sum of the oxides of carbon produced may exceed that of the methane by considerable amounts. It would probably not be profitable to follow up the investigation.

Discussion of the Results.

It must be pointed out in the first place that the thermal decomposition of dimethyl ether, and probably of compounds of the formula RR'O generally, takes place in two stages, each of which has peculiar characteristics, and that attempts to investigate either process by measuring the overall rate of decomposition cannot throw light on either.

The study of the primary decomposition process (equation 3) has been the particular object of this investigation, and the results appear to indicate that it is controlled by a number of factors the nature of which is very obscure. The main fact which emerges is that the primary decomposition of dimethyl ether into methane and formaldehyde may be slowed down by several processes, and actually brought to a complete standstill by the addition of very small quantities of nitric oxide. There appear to be two separate wall effects, but only one of these is counteracted by the addition of inactive gases such as hydrogen. There is also a process, operating in the gas phase, the nature of which is unknown which causes the sudden slowing down at the break-point. The mechanism of this process may, however, be similar to that of the action of nitric oxide, in which the slowing down of the main reaction involves the initiation of a secondary reaction, as in the case of the thermal decomposition of methyl nitrite.[8] Nitric oxide does not catalyse the primary decomposition process.

The form of the x/t graphs approaches much more closely to that representing a normal bimolecular process than do those representing the decomposition of ethane or acetaldehyde, and the only characteristic which they have in common with the latter is the occurrence of the breaks. One might be inclined to the view that the processes were therefore fundamentally different, and that there was no background reaction, to which can be attributed, at least mainly, the acceleration of the reaction. In this connection reference may be made to the fact that, while in the case of the hydrocarbons the background reaction involves a chemical process which can be studied separately, and in the case of acetaldehyde and acetone it may be represented by a well-recognised enol-keto change, in the case of dimethyl ether it is necessary to postulate a change which must involve the formation of a compound $CH_2 : OH . CH_3$ to account for a background reaction. However, it must be admitted that some such change must precede the formation of methane and formaldehyde, unless it is assumed that the process takes place through the action of free hydrogen atoms, which seems to be even less likely. A similar assumption has to be made to account for the thermal decomposition of methyl amine, where a second form having the formula, $CH_2 : NH_3$ must be assumed to exist. The thermal decomposition of dimethyl ether and of methyl amine are exceedingly sensitive to surface effects; but the thermal decomposition of methyl amine follows, otherwise, so closely on the lines of the thermal decomposition of acetaldehyde as to lead to the conclusion that the underlying mechanism of the two processes must be closely similar. However, it will generally be admitted that the forms $CH_2 : OH . CH_3$ and $CH_2 : NH_3$ are not normally tautomeric.

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[8] *This Journal*, p. 749.

It has been assumed in the previous papers dealing with thermal changes of this kind that the main reaction is in each case initiated by binary collisions of different molecular species, or tautomeric forms, related through the background reaction. The collision of molecules A and B must lead to an active complex AB, which, in turn, changes to the unstable intermediate. The energetic and steric properties of the complex AB must be the same whether it is formed at the first instant, or at any stage of the process. The slowing down of the process must involve the destruction of the complex, the complete stoppage of the reaction, as by the addition of NO, the complete extinction of the complexes as formed. It seems likely that the difference in the nature of the background reaction,

$$A \rightleftharpoons B,$$

and therefore the intrinsic difference in the character of the active complex in the case of dimethyl ether and of methyl amine on the one hand, and of ethane, acetaldehyde, etc., on the other may account for the differences in the behaviour of the two classes of compounds.

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THE THERMAL DECOMPOSITION OF CALCIUM AZIDE.

By D. J. B. Marke.

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The thermal decomposition of crystalline calcium azide, CaN_6, has been investigated by Andreew over the range of temperatures, 60°-150° C.[1] Nitrogen is liberated during the reaction and the final solid residue has the approximate composition, CaN_2. The decomposition takes a normal trend in that it gives an induction period followed by an acceleration of the reaction. Andreew working with 0·1 gm. of material in each experiment and using an ordinary mercury manometer for the measurement of pressures, showed that the equation, $dp/dt = kp^n$ held during the period of acceleration, n being about 0·66 for temperatures up to 100° but increasing to 0·80 for higher temperatures. Since in experiments on other exothermic decompositions, it had been found[2] that $n = 1$, the work of Andreew indicated that calcium azide was behaving differently from other exothermic solids. This difference between calcium azide and other solids is of some importance since conclusions have been drawn from the value of n as to the nature of the mechanisms of the solid reactions. The rate of solid decomposition will be given by equation (1)

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[1] *Physik. Z. Sowjet Union*, 1934, 6, 121.

[2] Garner, Gomm and Hailes, *J.C.S.*, 1933, 1393.

$$dp/dt = kp^{2/3} \quad . \quad . \quad . \quad . \quad (1)$$

only if certain conditions concerning the nuclei hold. These are (*a*) the nuclei must be all of the same size, (*b*) the rate of growth of the nuclei must be constant throughout, and (*c*) the reaction must occur on the surface of the nuclei at a rate proportional to their external area. Experiments on the rate of formation of nuclei on the surface of unscratched crystalline hydrates have shown that in the cases of copper sulphate pentahydrate and chrom alum the number of nuclei increase linearly with the time and in the case of nickel sulphate pentahydrate as the square of the time,[3] so that in the only cases where systematic measurements have been made, (*a*) does not hold. Experiments on the rates of growth of dehydration nuclei have shown that when above a certain size these rates are linear but that abnormalities occur when the nuclei are small, and in the case of chrom alum, an exponential rate of growth has actually been observed. Thus, on account of departures from the conditions (*a*) and (*b*), equation (1) cannot hold in all cases of solid decomposition. Conditions (*a*) and (*b*) are best realised when working with well-scratched crystals for under such circumstances large numbers of nuclei are present from the start of the experiment and these are probably of large size.

The chain theory of solid decomposition was put forward by Garner and Hailes,[4] and it was assumed by them that in the initial stages of the reaction, the reaction took a branching course throughout the solid either along cracks or among the discontinuities of the solid lattice. This would give rise to " diffuse " nuclei in contrast to the " solid " nuclei observed in the dehydration of hydrates. In the early stages of growth, since all of the molecules of the product are in contact with unchanged material, it would be expected that the rate of reaction would be proportional to the mass already decomposed, *i.e.*

$$dp/dt = kp \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Also, it follows that

$$\log dp/dt = k_1t + const. \quad . \quad . \quad . \quad (3)$$

and

$$\log p = k_1t + const. \quad . \quad . \quad . \quad . \quad (4)$$

should also hold. These equations have been shown to be in agreement with rates of decomposition of a number of exothermic solid reactions.

The relationships to be expected depend on the structure of the nuclei, n (equation 1) = 0·67 for compact nuclei under certain conditions and $n = 1$ for diffuse nuclei. It is possible that intermediate cases exist where n lies between 0·67 and 1·0 and that calcium azide is one of these. Experiments have been carried out with calcium azide to determine if this be the case.

Experimental.

Preparation of CaN_6.—Hydrazoic acid was passed into a solution of lime in water made from calcite and the calcium azide formed recrystallised from water. Aggregates were obtained consisting of small crystals which on analysis gave 96 per cent. of the theoretical quantity of N_2, and possessed a similar composition to that used by Andreew.

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[3] Bright and Garner, *J.C.S.*, 1934, 1872; Garner and Southon, *J.C.S.*, 1935, 1705; Cooper and Garner, *Trans. Faraday Soc.*, 1936, **32**, 1739.

[4] *Proc. Roy. Soc.*, *A*, 1933, **139**, 576.

Experimental Procedure.—A few milligrams of the azide were suspended in a platinum bucket in a part of the reaction vessel kept at room temperature,[4] and after evacuation for twelve hours, lowered into that part of the vessel kept at the required temperature. The range of temperatures covered was 80°-110° C. The reaction vessel was separated from the McLeod gauge by a liquid air trap to prevent interaction between mercury vapour and the products of the reaction. The nitrogen liberated was allowed to flow into a calibrated volume and the pressure was measured at intervals. It was possible to increase the volume of the measuring vessels by means of two calibrated expansion bottles, and use was made of these when the pressure became too large for the gauge. Experiments were carried out with whole and ground crystals.

Experimental Results.

The percentage of nitrogen liberated ranged from 67 per cent. to 87 per cent. (see Table I.). The weights of the crystals were only known to ± 0·1 mgm. If CaN_2 were the final product, 2/3 of the nitrogen should be liberated as molecular nitrogen and since in every experiment the volume liberated is greater than this, it is possible that a portion of the azide is converted into metallic calcium.* Typical pressure-time curves are given in Fig. 1 (i) and Fig. 2 (i). These are similar in form to those obtained with mercury fulminate and barium azide. The pressure increases as a high power of the time; n in the equation $p = t^n +$ constant varies with the time and lies between 3·5 and 6·0. This shows that there is some abnormality of nuclear growth.[2]

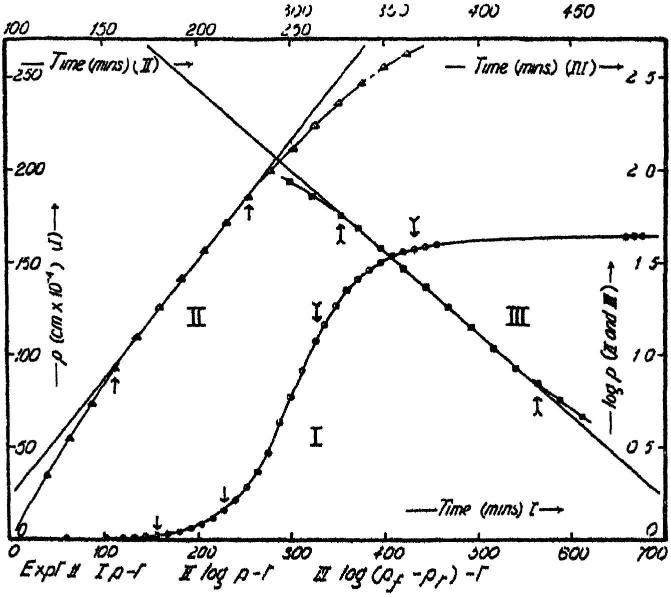

FIG. 1.

Test of the Chain Theory.

A few experiments were carried out with whole crystals (Table I.) and these gave a good agreement with equation (4), (Fig. 2 (ii)). The values for the acceleration constant, k_1, however, varied widely from experiment to experiment, so that a portion of the crystals was ground in an agate mortar and the powder thoroughly mixed. This did not, however, remove the causes of the irregularities in the values of the reaction constants. The results for a typical case of the ground material are shown in Fig. 1. Here equation (4) is only obeyed over the limited range given by the arrows on curve 1. It is clear that in this case the chain theory in its simple form is not in very good agreement with the results obtained. In this respect calcium azide differs from mercury fulminate, which gives good agreement with equation (4), both for whole and ground crystals. It is possible that the changes in the crystal structure of calcium azide brought about by grinding may mask the simple relationships previously found to hold with single crystals.

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* The presence of metallic calcium was indicated by the rapid whitening of the black residue in air.

The final stages of the reaction obey equation (5),

$$dp/dt = k_2(p_f - p_t) \quad . \quad . \quad . \quad . \quad (5)$$

where p_f is the final pressure and p_t that at time t, and this shows that the velocity is proportional to the mass undecomposed. A relationship of this kind would be expected to hold if the unchanged calcium azide were dispersed in a fine state of division throughout the solid and this state of affairs would result if the reaction obeyed a chain mechanism. Equation (5) holds for the latter stages of the decomposition of mercury fulminate, barium azide and lead styphnate, and Andreew shows that it holds for calcium azide also. It is thus of fairly general applicability in exothermic solid reactions. A test of (5) is made in Fig. 1 (iii) and the agreement is within experimental error. A further test was made of the unimolecular law by means of the equation $dp/dt = k_2(p_f - p_t)^n$ and in five determinations the average value of n was 1·08. There are, however, irregular variations in n due to some factor not under control; n varies between 0·9 and 1·2. The results show that the unimolecular law is obeyed approximately.

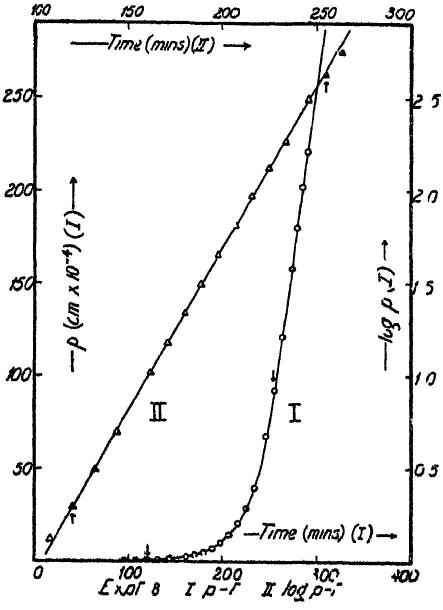

FIG. 2.

A summary of the constants in equations (4) and (5) and the values of $p_0 k_1^2/m$ is given in Table I. for the experiments on whole and ground crystals. p_0 is the antilog of the constant in equation (4) and m is the mass of the calcium azide taken. On the basis of the chain theory, $p_0 k_1^2/m$ is proportional to the rate of formation of nuclei. Grinding has but a slight effect on k_1 or k_2 and this is also the case for mercury fulminate. $p_0 k_1^2/m$, however, is increased 50-100 times by grinding and this effect is much less than that found for fulminate, *viz.* 10^8 times.

Activation Energies.—Andreew[1] mentions that the individual value of the constants for the reaction varied widely and that the activation energy could only be obtained by measurements on the same sample at two temperatures. He records the following values: 61-81°, 21·1 K.Cal.;

TABLE I

(mgm.).	Temp. °C.				Per Cent. Nitrogen Evolved
Whole crystals.					
2·4	109·2	2·40	[illegible]		
2·3	108·7	1·53	-		
2·5	108·1	3·34	3·81		
3·2	98·6	2·66	0·87		
10·05	111·1	5·06			
18·6	99·7	1·75			
Ground crystals.					
1·5	98·0	1·57	1·37	41·0	78·5
3·2	93·0	1·25	[illegible]	6·4	79·1
3·1	91·6	1·20	0·89	5·0	67·2
3·2	88·2	1·23	0·66	2·7	78·7
4·1	84·2	0·75		0·8	67·8
3·0	88·8	0·93	0·48	7·6	72·7
2·2	88·1	0·99	0·44	8·7	81·4
3·4	85·5	1·06	0·39	2·4	87·2
2·7	94·0	2·00	0·86	15·9	76·4
3·2	97·9	2·60	0·80	40·2	
2·4	93·9	1·66	0·56	28·9	-

* Assuming CaN_6 as formula for the azide.

81-61°, 20·8 K.Cal.; 100-80°, 22·1 K.Cal.; 106-93°, 27 K.Cal. The experimental values for log k_1 and log k_2 given above for the ground azide when plotted against $1/T$ give a somewhat broad band (Fig. 4). The same sample of ground azide was used throughout and the variation in the values

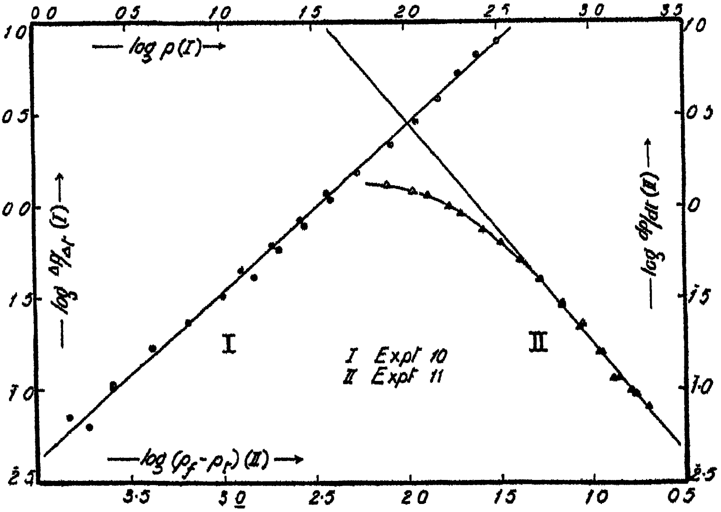

FIG. 3.

of the constants k_1 and k_2 cannot be due to differences in the physical state. Experiments are to be carried out to determine the causes of such variations. By the method of least squares, the values 18 K.Cal. and 19 K.Cal. are obtained from the values of k_1 and k_2 respectively. The agreement between these and those of Andreew is as satisfactory as could be expected since wide variations are met with from one sample to another. An estimation of the activation energy of nuclear formation gives a much greater value, *viz.* 77 K.Cal. and a similar value to this was obtained by Harvey for barium azide, *viz.* 80 K.Cal.

The fact that the activation energies for the initial and final stages of the reaction are practically identical is of some importance since it shows that the same chemical process is involved in all stages of the reaction. The activation energy for calcium azide is very similar to that of barium azide (*viz.* 21 K.Cal.) and is in marked contrast to the values for lead, potassium and sodium azides.[5]

Tests of the Applicability of Equation (1).—In view of the poor agreement found for the ground azide with equation (4), log dp/dt was plotted against log p and the values of n determined. A straight line is obtained (see Fig. 3 (i)). The values of n, however, lie between that demanded by the compact nuclei theory, *viz.* 0·67, and that demanded by the chain theory, *viz.* 1·0 (Table II.). This may indicate that the nuclei in the case of calcium azide are of an intermediate character possessing a solid core but being diffuse on the exterior.

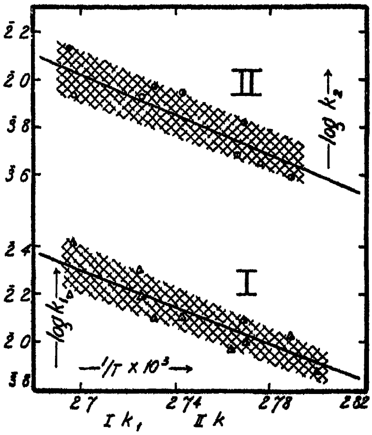

FIG. 4.

The irregularities met with in the case of the decomposition of crystals of calcium azide are very marked. These cannot be due to variations in the physical state of the solid, for the same sample of ground azide was used throughout. Nor could they be traced to the effects of exposure to light. It may be that they are due to the irregular heaping up of the solid in the platinum bucket. If this is the case, there must be some factor, which has not yet been taken into account in the study of solid decomposition, such as the effect of the products of the reaction, *e.g.* nitrogen atoms, on the reaction rate.

TABLE II.

Temp. °C.	$k \times 10^2$.	–
84·2	1·95	0·91
85·5	3·01	0·86
88·1	3·35	0·80
88·2	3·31	0·85
88·8	3·18	0·79
91·0	3·59	0·80
93·0	3·57	0·91
93·9	5·04	0·87
94·0	5·12	0·89
97·9	9·14	0·76
98·0	4·22	0·89

Summary.

. The results obtained by Andreew on the thermal decomposition of calcium azide have been confirmed. The activation energy of this reaction was found to be 18-19 K.Cal. approximately, for the range of temperatures, 80°-100° C. This is about half as great as those for potassium, sodium, and lead azides, but is of the same order as for barium azide. The activation energy calculated for nuclei formation is approximately 77 K.Cal.

The rates of decomposition are in general agreement with those expected from the chain theory, but in the case of ground calcium azide, n in the equation $dp/dt = kp^n$ lies between 0·75 and 1·0, indicating that the

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[5] *Cf.* Garner and Marke, *J.C.S.*, 1936, 657, where this matter is discussed.

nuclei formed are not so diffuse as those usually found in exothermic solid reactions.

The author is deeply indebted to Professor W. E. Garner for his help and advice and to the Department of Scientific and Industrial Research for the grant which has enabled him to carry out this work.

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VARIATION WITH TEMPERATURE OF THE ULTRA-VIOLET ABSORPTION SPECTRA OF ACETONE AND IODINE IN SOLUTION.

By H. J. Walls and E. B. Ludlam.

Received 26th February, 1937.

Hitherto, the effect of temperature on the absorption spectrum of a substance in solution has been little studied.[1-5] The investigation of the variation should be instructive in regard to the several factors which may be expected to determine the absorption both of the solvent and of the solute. The choice of solvent is limited in that it must have a low freezing-point and be transparent in the region in which the solute absorbs.

We have examined the absorption of solutions of two substances which have already been carefully studied in the pure state at ordinary temperatures and show maxima at convenient wave-lengths, 2800 Å. for acetone and 2900 and 3600 Å. for iodine. As solvents hexane, methyl alcohol and water have been used.

Since this work was undertaken an interesting paper has been published by Bloch and Errera,[6] who have examined the change with temperature in the infra-red absorption of a number of characteristic pure organic substances, including acetone, and have found that, with the exception of the band due to —OH, there was no measurable variation.

The various factors which determine the precise position, magnitude and shape of the absorption curves will be: (1) the *electronic transition*, which locates the band (*e.g.* 2800 Å. for the —CO band). (2) The *nature of the solvent* and particularly the influence of its polarity on the electronic transition. (3) The *vibrational* states of the solute, which will determine the shape of the curve. (4) *Association* of the solute which will affect the magnitude of the absorption. (5) The effect of temperature on each of the above. (6) Photochemical change, which however may be neglected when the exposure is short and the source of light not too powerful.

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[1] Scheibe, *Ber.*, 1925, 58, 586.

[2] Scheibe and Lederle, *Zeitschr. f. ph. Ch.*, *B*, 1929, 6, 247.

[3] Mukerji, Bhattacharji and Dhar, *J. Physic. Chem.*, 1928, 32, 1834.

[4] Arnold and Kistiakowski, *J. Amer. Chem. Soc.*, 1932, 1713.

[5] Trehin, *Journ. Phys. et le Rad.*, *VII*, 1933, 4, 430.

[6] Bloch and Errera, *ibid.*, 1935, 6, 154.

Experimental.

Materials.—A.R. acetone was used without further purification. The hexane was the British Drug Houses' hexane "specially purified for spectroscopy," which had been found entirely satisfactory for this work. The methyl alcohol was "absolute," dehydrated with magnesium,[7] then redistilled, large first and last portions being rejected. A 1 mm. layer of the sample used transmitted freely to 2100 Å.; a 40 mm. layer to 2250 A. The water used was conductivity water degassed under vacuum. (This precaution is advisable to prevent bubbles forming inside the cells used for measurement.)

Apparatus.—All measurements were made by the usual method of comparative spectra, using a Bellingham and Stanley rotating sector photometer and "medium" quartz spectrograph, with an iron spark as light source.

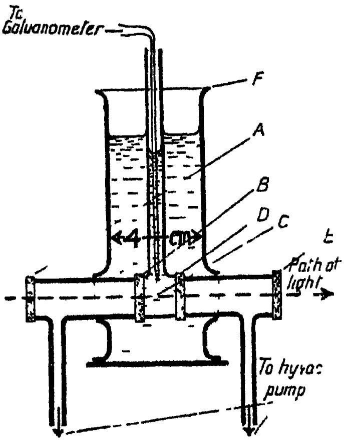

FIG. 1.

For the temperature control of the solutions two forms of containing cell were used. The first was a very simple "thermo-siphon." The whole was made from silica; the cell had plane parallel ends and was about 1 cm. in length. Its exact internal length was found by measuring the apparent absorption of a solution of KBr whose absorption was also measured in a cell of known length. Part of the tube was wound with resistance strip and covered with asbestos. On filling with the solution to be measured, and passing a current through the resistance strip, a convection circulation was set up, and, in a position free from draughts, equilibrium, as indicated by constant temperature of the solution in the cell, was reached in about half-an-hour. The temperature in the cell was measured by means of a copper-constantan thermo-couple, used with a galvanometer and scale giving a sensitivity of about 6 mm. scale deflection/° C. As no perceptible diminution of volume occurred during measurement even with hexane at 50° C., any change of concentration due to evaporation may safely be neglected.

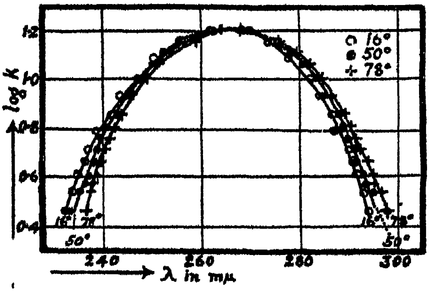

FIG. 2.—Temperature Variation of Absorption Spectrum of Acetone in Water.

As this form of apparatus was not suitable for measurements at low temperatures, a different form was used for this (Fig. 1). It did not permit of the very accurate temperature control achieved by Arnold and Kistiakowsky,[4] but was extremely simple. The cell C was again about 1 cm. in length (measured with a micrometer before assemblage). A, B, D, E were circular quartz plates about 1-2 mm. in thickness, and the tubes AB, DE and the cell had their ends ground plane and parallel to fit on to these. The plates A and E were secured with picein, and the joints at B and D were covered with liquid glue applied externally and allowed to harden. This produced a joint sufficiently vacuum-tight, did not contaminate the liquid in the cell, and was insoluble in the cooling liquid. Other joints were made liquid-tight with a mixture of water-glass and asbestos, and a small block of plaster of Paris cast around the lower part of the tube F secured mechanical strength. The whole was well insulated with cotton-wool. For a measurement the cell C was filled with the solution and the tube F filled with the cooling liquid, usually CO_2 snow and ether; the tubes AB and DE were evacuated; two small electrically-heated coils were placed so that the ascending currents of warm air prevented the condensation of moisture on the outer surfaces of A and E. The temperature could be kept constant to ± 1° at − 65° for half-an-hour

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[7] Bjerrum, *Ber.*, 1923, **56**, 894.

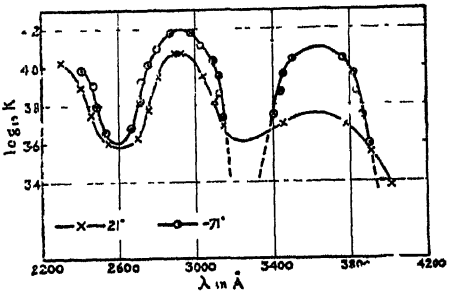

FIG. 3.—Temperature Variation of Absorption Spectrum of Iodine in Ethyl Alcohol.

TABLE I.

	Solvent for Acetone.	Concn. mols./litre.	Temp. °C.	$\lambda_{max.}$ in A.	Log $k_{max.}$ (corrected).	
1	Water .	0·0675	16	2648	1·21	
2		0·0675	50	2651	1·21	
3		0·0675	78	2661	1·21	
—		0·1598	Normal ?	2645	1·24	Scheibe.
4	Methyl Alcohol .	0·0702	17	2701	1·19	
5		0·0702	50	2715	1·20	
6		0·102	−69	2677	1·25	
7		0·102	20	2703	1·24	
—		0·1405	Normal ?	2700	1·19	Scheibe.
8	Hexane .	0·0675	13	2773	1·16	
9		0·0675	50	2787	1·15	
10		0·0819	1	2771	1·065	
11		0·0819	35	2781	1·125	
12		0·0819	49	2789	1·15	
13		0·0967	−66	2753	1·21	
14		0·0967	22	2775	1·16	
—		0·1464	Normal ?	2790	1·17	Scheibe.
—	Heptane .	ca. 0·1	Normal ?	2785	1·23	Rice.
—	Liquid Acetone .	—	Normal ?	2747	—	Rice.
—	Acetone Vapour .	—	Normal ?	2800	—	Bowen and Thompson[10]
15	Iodine in Ethyl Alcohol	0·0000902	21	2921 and 3630	4·07 and 3·75	
16		—	−71	2940 and 3640	4·21 and 4·11	

without difficulty. With this apparatus, a correction had to be applied on account of the fact that the cell containing the solvent had only four quartz surfaces in the path of the light, whilst the apparatus containing the solution had eight. As the extra absorption resulting was dependent on λ, the correction to be applied was found by measuring the absorption at various λ's when both cells were filled with the pure solvent.

Results.—As the absorption spectra curves of acetone in solution are familiar, the actual λ-log (extinction coefficient) curves obtained with this solute are not reproduced, except those for water as solvent, which are shown as an example of the results obtained (Fig. 2). (The correction for thermal expansion—see below—has not been applied to the curves in this figure.)

The results obtained are embodied in Table I., where some of the previous results of Scheibe [1] and Rice [8] are also included for comparison. The figures in Table I. also agree substantially with those of Wolf.[9] The positions of $\lambda_{\text{max.}}$ given are found by Scheibe's method,[1] *i.e.*, they are in each case the intersection of the absorption curve and the line joining the middle points of "chords" parallel to the wavelength axis. The values of log $k_{\text{max.}}$ ($\log_{10}$ extinction coefficient at λ of maximum absorption) given have been corrected for the change in concentration produced by the thermal expansion (or contraction) of the solvent. The values of the coefficient of expansion for the pure solvent were used for this, as the error involved in applying it to solutions will be extremely small at the concentrations used. The maximum variation of temperature during any measurement was about ± 1·5°, and for the majority of cases it was not more than 0·5°.

In Table II. the actual frequency change is correlated with the temperature change.

TABLE II.

	Solvent for Acetone.	Concn. mol./litre.	$\nu_{\text{max.}}$ (cm.$^{-1}$).	Temp. °K (T).	$\Delta\nu$.	$\Delta\tau$.	$\Delta\nu/\Delta\tau$.
1	Water .	0·0675	37770	289	50	34	1·5
2		0·0675	37720	323	140	28	5·0
3		0·0675	37580	351			
4	Methyl Alcohol .	0·0702	37010	290	180	33	5·5
5		0·0702	36830	323			
6		0·102	37340	204	350	89	3·9
7		0·102	36990	293			
8	Hexane .	0·0675	36060	286	190	37	4·5
9		0·0675	35880	323			
10		0·0819	36080	274	120	34	3·5
11		0·0819	35960	308	100	14	7·1
12		0·0819	35860	322			
13		0·0967	36330	207	300	88	3·4
14		0·0967	36030	295			
15	Iodine in	0·902 × 10^4	34230 27550	294	220 (λ	92 max. 2	2·4 900)
16	Ethyl Alcohol .	0·902 × 10^4	34010 27470	202	80 (λ	92 max. 3	0·85 600)

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[8] Rice, *J. Amer. Chem. Soc.*, 1920, **42**, 727.
[9] Wolf, *Z. physik. Ch.*, *B*, 1929, **2**, 39.
[10] Bowen and Thompson, *Nature*, 1934, **133**, 571.

Discussion.

From the results of Bloch and Errera[6] for acetone, that the =CO band at 1·98 μ remains unchanged over a temperature range from + 20 to − 70° C., we may assume that the part played by the vibration-rotation energy may be neglected in considering the cause of the shift in the ultra-violet shown in Tables I. and II. We need then only consider (1) solvent effect and (2) effects of association of the solute.

Changes in ultra-violet absorption have long been satisfactorily ascribed to polar or electrostatic effects. When the temperature is also varied the increased thermal agitation produced by a rise in temperature, will, in the case of a polar solvent, tend to destroy the orientation of the dipoles, and hence reduce the deforming effect of these on the electron system. Hence, *increase of temperature should produce the same effect as a decrease in polarity of solvent, i.e. a shift of the absorption maximum towards the red.* Table I. shows that this actually occurs in the case of acetone. Table II., column 8, shows that the shift for equal temperature intervals is least for water. *A priori*, we might have expected it to be least for the non-polar hexane, as in this case there can be no change with temperature of the influence of solvent dipoles. However, the fact that the maximum is shifted to a shorter wave-length in water, as compared with hexane at normal temperature, shows that more energy is required in aqueous solutions to effect the electron transition. If the position of maximum absorption depends on the resonance of the electron which enables it to pick up energy of definite frequency, then the shift must be due to a change in the frequency of maximum resonance, and with this change of frequency is associated a change of energy absorbed. In any case more energy will be required to effect the transition in the aqueous solution, and so it is not surprising that the temperature effect should in this case be correspondingly smaller.

A complication is introduced by the fact that we do not know the ratio of the temperature coefficients for water-water and water-acetone association. *E.g.* if water-water association is predominant at low temperatures, and if as the temperature is raised the dissociation of water-acetone complexes is hindered by a dissociation of water, which, by yielding a greater supply of unassociated water molecules tends to reverse the other process by a mass action effect, then we have here another reason for the low value of $\Delta\nu/\Delta T$ in the case of water.

Further, accepting Scheibe's statement[1] that acetone in water (and probably in the alcohols) obeys Beer's Law while in hexane it does not, this means that the polar solvents entirely prevent the association of acetone molecules at quite high concentrations, so that the acetone is even at these concentrations in condition corresponding to infinite dilution. In hexane, however, this will not be the case. Hence, for similar temperature ranges, we should expect $\Delta\nu/\Delta T$ to be independent of temperature in polar solvents but not in non-polar solvents. While there is just an indication that this may be the case (Nos. 10, 11, and 12 in Table II.), the data available do not enable us to settle this point.

Another feature which Table II. brings out is that the value of $\Delta\nu/\Delta T$ seems to increase with increasing temperature: see Nos. 1, 2, 3; 4, 5; 6, 7; 10, 11, 12. (The figures for methyl alcohol for the temperature intervals 290° K.-323° K. and 204° K.-293° K. refer to different concentrations, but if, as Scheibe states, acetone in methyl alcohol obeys Beer's Law, the comparison is just.) This points to a rate of change of association with temperature increasing as the temperature increases, which is not unlikely; but there are insufficient data on which to base speculation.

In view of the fact that energy absorbed by the C=O group can under certain circumstances be transferred to (and produce disruption of), another part of the ketone molecule,[11, 12] a simple calculation may be made showing that this "activation," even if it takes place, must be unimportant. The observed change of wave-length is several times as great as could be produced by a "temperature activation" alone, even making the unlikely assumption that all the energy available goes as a contribution towards the electron transition.

As Bloch and Errera found no change at low temperature in the vibration-rotation absorption in pure acetone it would appear that there is no change in the vibrational quantum and no change in the distribution of the rotational quanta.

In the case of iodine in solution in ethyl alcohol, both maxima are shifted to *shorter* wave-lengths with rise of temperature (Table I.)—*i.e.* the shift is in the opposite sense to that in the case of acetone. We have, however, no data at present for the longer wave-lengths, corresponding to those of Bloch and Errera for acetone, to guide our consideration of possible causes in the case of iodine, which shows a much greater change with temperature in the value of log $k_{max.}$ (Table I.).

The change in $\lambda_{max.}$ cannot profitably be discussed here since there are too many unknown factors which might affect it. The general form of the curves, however,—a narrowing of the bands and increase of log $k_{max.}$ with decrease of temperature—can be simply explained by assuming that at low temperatures the iodine possesses very few vibrational quanta, and that the electron transition can only be from a few of the lowest vibrational levels in the normal state to the appropriate vibrational levels in the higher electronic state.

Summary.

1. The absorption spectrum of acetone in solution in water, methyl alcohol, and hexane has been measured at various temperatures over a range of about 150° C.

2. In all solvents the maximum of absorption shifts towards the red with increase of temperature.

3. The shift is much less for water than for the other solvents; and in all the solvents the ratio, shift/(temperature difference), appears to increase with rise of temperature.

4. These effects are briefly discussed.

5. Iodine in ethyl alcohol shows a shift to shorter wave-lengths with rise of temperature.

The above work was carried out in Edinburgh University. We should like to express our thanks to I. C. I. Ltd. for a grant with which the photometer was purchased, and to Miss Maclean and Mr. Tebrich for measurements of the coefficient of expansion of hexane at temperatures from − 70° C. to 0° C. One of us (H. J. W.) is also indebted to the Carnegie Trust for a research scholarship held while the above work was being carried out.

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[11] Norrish, *Trans. Faraday Soc.*, 1934, **30**, 103.
[12] Norrish and Saltmarsh, *J. Chem. Soc.*, 1935, 455

QUALITATIVE INVESTIGATION OF THE EFFECT OF OXYGEN ON THE POWER OF TUNGSTEN TO DISSOCIATE HYDROGEN.

By George Bryce.

Received 3rd March, 1937.

When tungsten is heated to over 1000° K. in a mixture of hydrogen and oxygen the oxygen is first preferentially consumed,[1] and it is only some ten to fifteen minutes after the disappearance of this gas that the normal hydrogen dissociation starts. Attempts have been made to account for the time lag preceding the hydrogen dissociation by assuming that an adsorbed unilayer of oxygen atoms must first begin to evaporate before hydrogen molecules can reach the clean metal surface and be dissociated. The object of the present work was to examine the effects separately by first introducing oxygen, and then testing with hydrogen after residual oxygen had been removed from the gas phase. The hydrogen atoms were detected by using the sensitive method already described.[2]

The apparatus was the same as before,[2] and the reaction bulb was kept at 0° C. In several experiments, after the usual cleaning by flashing in vacuo, the tungsten was exposed at 0° C. to oxygen at pressures up to 2 mm. Hg. After the oxygen had been pumped out tests showed that in each case normal rates of hydrogen dissociation were obtained over the short time intervals employed.[*] It is known[3] that the tungsten surface would in the absence of hydrogen remain 92 per cent. covered with oxygen atoms by exposure at 0° C. to even lower pressures of molecular oxygen,[†] but at these temperatures hydrogen may be able to remove this oxygen film.

In a number of experiments by other workers tungsten has been covered with oxide by heating it to a high temperature in low pressures of the gas.[4] The effect of this treatment has been tried. It is well known that surface oxide, or oxides, form when tungsten is heated at temperatures less than 1000° K. in oxygen. Previous work suggested[5] that no bulk oxide would remain on the surface after heating to over 1000° K. *in vacuo*, and hence, after treatment in oxygen, the filament was always heated to 1300°-1400° K. *in vacuo*, these temperatures not being high enough to cause evaporation of the adsorbed atomic layer of oxygen. When the metal was heated to 1000°-1800° K. in 10^{-3} mm. Hg. pressure of oxygen for a few seconds, very little change in the power of the wire for dissociating hydrogen was found. Longer heating at 1400° K., or lower temperatures in oxygen at less than 10^{-2} mm. Hg. pressure made the wire less active, but its activity in causing hydrogen to dissociate depended markedly on the previous treatment in oxygen. Indeed the wire could be completely poisoned * by heating for five minutes at 1400° K. in oxygen at 0·1-0·2 mm. Hg. pressure, and remained so even when subsequently heated *in vacuo* for ten minutes at 1400° K.

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[1] Langmuir, *Chemical Reviews*, Baltimore, p. 147 (1933). A summary of, and references to, all Langmuir's work on the subject will be found here.

[2] Bryce, *Proc. Camb. Phil. Soc.*, 1936, **32**, 648.

[*] The duration of an experiment varied from ten minutes at 1148° K. to one minute at 1420° K.

[3] Roberts, *Proc. Roy. Soc.*, 1935, **152**, 464.

[†] The immobility of the atomic film of oxygen on tungsten leads to about 8 per cent. of isolated tungsten atoms in the surface being unable to adsorb oxygen as atoms. Over these gaps in the atomic film oxygen molecules are adsorbed with a heat of adsorption of 48 k. cals, so that in the above experiments the molecular film was probably very rapidly evaporated, leaving the tungsten surface 92 per cent. covered with oxygen atoms.

[4] Langmuir and Villars, *J. Amer. Chem. Soc.*, 1931, **53**, 486.

[5] Langmuir, *Trans. Faraday Soc.*, 1922, **17**, 607.

Since the poisoning was thus so variable (and depended, as Table I shows, on (1) the time of heating the tungsten in oxygen, (2) the oxygen pressure, and (3) the temperature of the metal), a reproducible surface did not result from so treating the metal, and the values given in Table I for the power imput required to maintain the filament at a given temperature *in vacuo* show that the emissivity is also variable, which suggests the presence of bulk oxide on the surface. After treatment at 1400° K. in 1 mm. Hg. pressure of oxygen the emissivity of the tungsten had increased, and it remained high during fifteen minutes heating at 1400° K. *in vacuo*. Then part of the filament suddenly glowed more brightly than the rest; at the same moment the emissivity started to fall, and continued to do so as the bright area spread.† When the wire with the uneven glow was cooled that part which had been brightest showed metallic lustre.

TABLE I.

Treatment of Tungsten Filament in Oxygen.			Power required thereafter to Heat to same resistance (1350°-1400° K) *in vacuo*.		State of Wire for Hydrogen Dissociation.
Temperature of Tungsten °K.	Duration of Heating min.	Initial Pressure of Oxygen mm. Hg.	Filament Heated *in vacuo* for min.	Watts Input.	
2400	10	In vacuo.	—	1·40	Active.
288	5	1	5	1·40	Active.
1400	1	5×10^{-2}	10	1·56	Partly poisoned.
1300	1	1	5	3·60	Poisoned.
2400	10	In vacuo.	—	1·13	—
1350	1	1×10^{-2}	5	1·15	—
1350	5	1×10^{2}	5	1·21	—
1350	0·5	0·2	5	2·54	—

It is important to point out explicitly that the behaviour just described was observed in the absence of hydrogen so that it was not connected in any way with the reduction of an oxide layer by hydrogen. As might be expected, similar effects were observed when, after the oxygen treatment, the filament was heated at 1400° K. in a low pressure of hydrogen.‡ It was only at the instant when part of the filament started to glow more brightly, and the emissivity to decrease, that the wire suddenly partly regained its power to dissociate hydrogen. The exact nature of the layer which makes the metal slightly duller, and causes a rise in its thermal emissivity, remains unknown, and was not revealed by X-ray analysis or by the electron diffraction method. The present experiments suggest that it is a residue of bulk tungsten oxide, or oxides, which takes a considerable time to leave the surface at 1400 K. *in vacuo*. It is this layer which prevents tungsten from dissociating hydrogen.

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* That is, the pressure did not change by more than 10^{-4} mm. Hg. in five minutes when a test at 1400° K. was made in hydrogen.

† A somewhat similar behaviour in which one spot of a platinum wire becomes active in catalysing the combination of carbon monoxide and oxygen, the activity afterwards spreading from this spot along the whole filament, has been observed by W. Davies (*Phil. Mag.*, **19**, 309 (1935)).

‡ Hydrogen is known to reduce tungsten trioxide at temperatures less than 1000° K. Under the present conditions, however, it was not markedly effective in freeing the poisoned filament from bulk oxide, which may be a mixture of some of the many oxides of tungsten which have been reported, and of which WO_2, W_2O_5, and WO_3 seem to be well established.

This work was made possible by the award of a Glasgow Ramsay Memorial Fellowship, for which the author is grateful to the Trustees. He also wishes to thank Professor Rideal and Dr. J. K. Roberts for their interest and help.

Summary.

The effects on the thermal emissivity and the power for dissociating hydrogen caused by heating tungsten in low pressures of oxygen have been studied. It appears that it is much more difficult to free the surface from bulk oxide, formed during heating in oxygen, than was supposed. The process of oxide removal proceeded similarly whether the specimen was heated *in vacuo*, or in low pressures of hydrogen.

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THE EFFECT OF PROMOTERS ON MOLYBDENUM CATALYSTS AS USED IN HYDROGENATION.

By F. E. T. Kingman.

Received 18*th March*, 1937.

In the hydrogenation-cracking * of coals, tars and similar materials, a noteworthy feature is the outstanding position as catalysts of molybdenum compounds, and in particular, of molybdenum sulphide. It has been suggested that the trisulphide is the active catalyst—the catalyst losing its activity as the trisulphide decomposes into the disulphide and sulphur. On the other hand, from the work of Parravano and Malquori [1] on the vapour pressure of sulphur from molybdenum trisulphide, it would appear that, under the normal conditions of hydrogenation experiments, the trisulphide would be completely unstable, and would be converted almost instantaneously to the disulphide.

In the beginning of this work attempts were made to confirm the results of Parravano and Malquori, using a dynamic method based on Knudson's effusion method as developed by Egerton,[2] and also a static method, similar in principle to that of Parravano and Malquori, but using the quartz spring balance of Bakr and McBain [3] to determine the change in weight due to the decomposition or formation of the trisulphide.

The results of these experiments indicated, however, that at the temperatures investigated (about 300° C.) molybdenum trisulphide does not exhibit a constant dissociation pressure of sulphur, for although at any given temperature it may appear to do so for a fixed ratio of molybdenum to sulphur, the dissociation pressure decreases with the decrease in the amount of sulphur present. This result, suggestive of the formation of a continuous solid solution of MoS_2 in MoS_3, is not necessarily in disagreement with that of Parravano and Malquori,[1] since they did not attempt to investigate the change in vapour pressure with change in the Mo/S ratio, and it does confirm the earlier conclusion, which has since been supported by direct experiment, by several workers, that under the ordinary conditions of hydrogenation-cracking molybdenum trisulphide is unstable.

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* *i.e.* treatment with hydrogen at high pressures (about 200 atmos.) and at temperatures of 350°-500° C.

[1] *Atti. Accad. Linc.*, 1928 (vi.), 7, 109.

[2] *Proc. Roy. Soc. A*, 1923, 103, 469.

[3] *J.A.C.S.*, 1927, 49, 1157.

X-ray diagrams of the molybdenum trisulphide before and after several hours' heating, showed that in addition to the chemical change represented by the conversion to the disulphide, there was also a marked change in the physical structure of the catalyst. The original trisulphide was extremely micro-crystalline, almost amorphous in character, whereas the heated material had a much larger particle size and gave an X-ray diagram similar to that of molybdenite (MoS_2). It will be shown later that the increase in particle size, with the consequent decrease in surface area, was accompanied by a decrease in catalytic activity.

These results furthermore suggested that a possible method of increasing the activity of molybdenum sulphide catalysts would be the introduction of promoter atoms, whose function would be to diminish the rate of sintering of the molybdenum sulphide. In the remainder of this paper a description is given of investigations which have been carried out to determine the general effect of promoters on the catalytic activity of molybdenum compounds.

Experiments with Promoted Catalysts.

The efficiencies of the catalysts were tested by measuring their activity in the conversion of phenol to benzene by hydrogen at atmospheric pressure. This reaction was chosen as being one of the reactions involved in the technical process for the hydrogenation-cracking of low-temperature tar, for which process molybdenum catalysts are more especially used.

Experimental Method.

Cylinder hydrogen, stored in a graduated holder, was passed through a purifier (heated palladium-coated copper for the removal of traces of oxygen) and a phosphorus pentoxide drying tube. The purified and dried gas passed through a capillary flow-meter, and then bubbled through a carburettor consisting of two wash-bottles in series containing phenol, and maintained at a constant temperature (generally 85·0° C.) by an electrically heated air bath. The mixture of phenol vapour and hydrogen then entered the reaction tube, which was heated by an electric furnace. The tubing between the phenol bubbler and the reaction furnace was maintained at about 200° C. in order to avoid condensation of the phenol, and to form a preheater. The tube containing the catalyst was constructed so that while fresh batches of catalyst could easily be inserted or removed, the position of the catalyst in the furnace was always the same. The temperature of the reaction tube was measured by a calibrated platinum-platinum-rhodium thermocouple.

The products of the reaction, consisting of benzene and water, together with any unchanged phenol, were condensed in a U-tube, cooled with liquid air. The U-tube was connected to the catalyst tube by a ground joint sealed with a layer of tin-foil, so that it could be removed, and the ends closed with stoppers for the weighing and analysis of the total product.

In carrying out an experiment, the apparatus was run under the desired experimental conditions for thirty-five minutes before the U-tube was fitted into position. The product was collected over a further period of one hour, the U-tube then removed and weighed. The product was washed out into a 100 c.c. graduated flask with successive washings of 10 per cent. caustic soda, followed by distilled water, the caustic soda ensuring the complete removal of the unchanged phenol. The solution was made up to 100 c.c. and aliquot portions then taken for determination of the unchanged phenol by the potassium bromate method.[1] The accuracy of the method and the solutions used was tested by analysing a solution containing a known weight of pure phenol.

The percentage of phenol in the product thus obtained was then converted to the percentage based on the original phenol by correcting for the increase in weight of condensible material caused by the reaction,

$$C_6H_5OH + H_2 = C_6H_6 + H_2O.$$

At the reaction temperatures used, very little conversion of benzene to cyclohexane could take place, so that errors due to the increase of weight of liquid product caused by this reaction may be safely ignored.

In order, as far as possible, to eliminate the deterioration of the catalyst by the deposition on the surface of high-boiling polymerisation products, the molecular proportion of hydrogen to phenol was maintained at about 50 : 1. Under these conditions the reaction can be treated as one of first order:

i.e. $$-\frac{dx}{dt} = kx \quad (x = \text{concentration of phenol}),$$

from which

$$kt = \log_e \frac{a}{a - x} \quad (a = \text{initial concentration of phenol})$$

and since α = percentage of phenol unconverted = x/a

$$kt = \log_e \frac{1}{1 - \alpha}.$$

In the experiments described below, for any one series, the throughputs of the hydrogen and phenol were constant, *i.e.* t is constant, and we have (for any given series)

$$k_1 = \log_{10} \frac{1}{1 - \alpha} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

From the change in k_1 with temperature, values of the apparent energy of activation for different catalysts can be calculated.

Results.

The first series of experiments was carried out with a molybdenum trisulphide catalyst, prepared by precipitation from a solution of ammonium thiomolybdate by dilute sulphuric acid. The catalyst was compressed into small pellets and 1·35 gm. of catalyst inserted in the reaction chamber. A throughput of phenol of 0·3 gm. per hour was used with a reaction temperature of 350° C. The results are shown in Fig. 1, where the efficiency of the catalyst, as measured by the percentage of phenol converted, is shown plotted against the total time of heating of the catalyst. The rapid decrease in activity is evident.

In the investigation of promoters, the substances first tried were silica and chromium and aluminium oxides, but these substances tended to decrease rather than increase the activity. It was found, however, that the catalytic activity of molybdenum sulphide was markedly enhanced by the co-precipitation, with the molybdenum trisulphide, of ammonium phosphomolybdate, and later experiments showed that ammonium phosphomolybdate itself gave a highly active catalyst.

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[1] Treadwell and Hall, *Analytical Methods*, 5th edn., Vol. 2, p. 695.

Experiments with Catalysts prepared from Heteropoly-Compounds of Molybdenum.*

In view of the results obtained with the catalyst prepared from ammonium phosphomolybdate, a series of catalysts was prepared from heteropoly-acids of molybdenum, both of the 12 acid and 6 acid groups, with the promoter atom as the central atom of the complex anion. In actual practice, the ammonium salt of the heteropoly acid was always prepared, and this was heated in hydrogen for six hours at 480° C., when the heteropoly acid was decomposed, and a catalyst consisting either of the mixed oxides of molybdenum and the promoting atom or of molybdenum dioxide and the promoting atom itself obtained. By this treatment, each catalyst was subjected to a fairly drastic and identical sintering process before testing its activity and the catalysts with high initial but transient activities were deactivated.

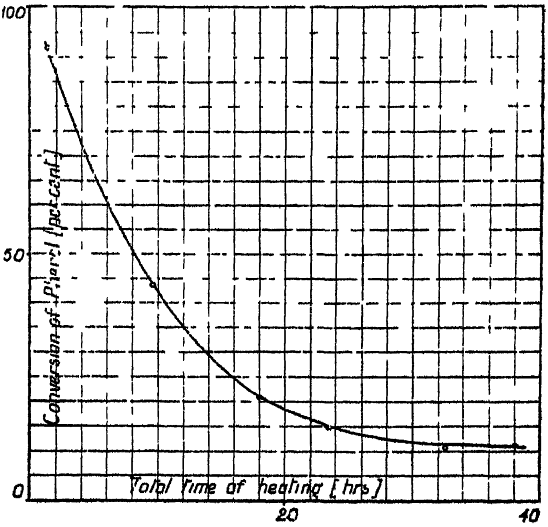

FIG. 1.

TABLE I.

Catalyst.	Promoter.	Activity (per cent. conversion of Phenol).
Mo oxide	Unpromoted	24·0
„	P	95·0 (mean of two experiments)
„	Si	78·5
„	Th	18·3
„	Sn	14·1
Mo oxide V oxide	P	51·9

Some preliminary experiments were first carried out, with 0·45 gm. catalyst and a throughput of phenol of 0·35-0·4 gm. per hour at a reaction temperature of 350° C. A brief summary of the results obtained is given below.

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* Ammonium phosphomolybdate is the ammonium salt of one of a numerous series of heteropoly-acids of molybdenum. These complex acids and their salts can be divided into two classes according to whether there are twelve or six molybdenum atoms grouped around the central atom of the complex, and can be represented by the following formulæ.[5]

1. 12 acid $R_n[X.(Mo_2O_7)_6]$ X = P, Si, As, Th, Sn, etc.
2. 6 acid $R_n[M.(MoO_4)_6]$ M = Cu, Ni, Cr, Co, etc.
R = H, NH_4, K, etc.

More recently Keggin and Illingworth [6] have shown by X-ray examination that the formula for phosphomolybdic acid (and possibly, therefore, of the other twelve acids) is of the type $H_{12}P(Mo_{12}O_{40})$, but the main classification of these compounds is not affected by this slight modification.

[5] Abegg, *Auerbach, Handbuch der anorg. Chem.*, Vol. 4, Part 1, second half, p. 977.

[6] *J.C.S.*, 1935, 1, 578.

All these promoted molybdenum oxide catalysts were prepared from heteropoly-compounds of the first group, *i.e.* with 12 molybdenum atoms to each promoter atom. The unpromoted molybdenum oxide catalyst was prepared from ammonium molybdate and the mixed molybdenum oxide-vanadium oxide catalyst with phosphorus as promoter was obtained from the mixed phosphorus hetero-poly compound of molybdenum and vanadium, prepared by the method described by Gibbs,[7] and according to him of the formula

$$8(NH_4)_2O . P_2O_5 . 8V_2O_5 . 14MoO_3 . 50H_2O.$$

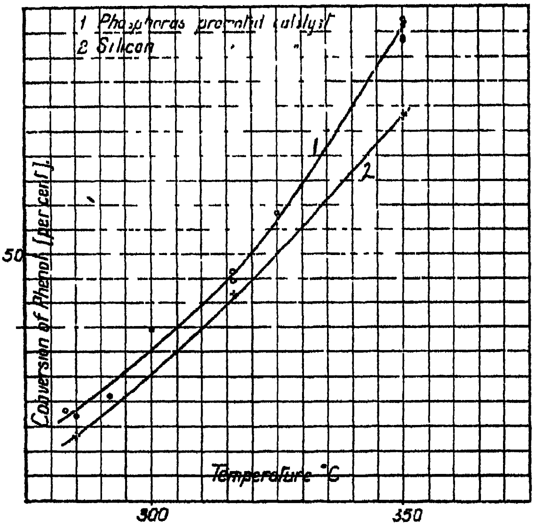

FIG. 2.

The results for the phosphorus and silicon promoted catalysts over a range of temperature of 280°-350° C. are shown in Fig. 2. The results for the phosphorus promoted catalyst were obtained from experiments with two separate batches of catalysts.

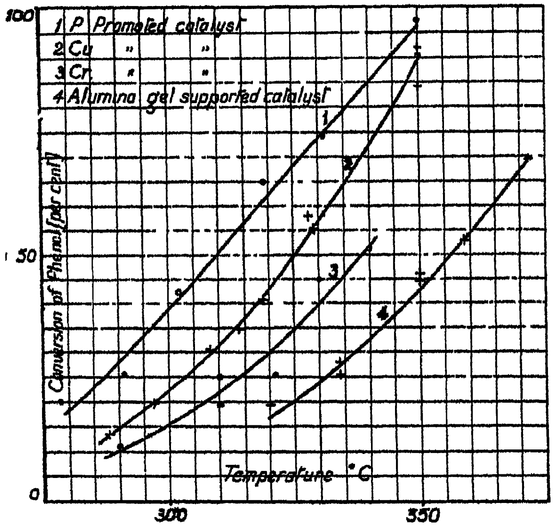

FIG. 3.

The investigation was then extended to the catalysts prepared from the second group of heteropoly compounds. In view of some erratic results obtained when using only 0·45 gm. of catalyst, it was decided to increase the weight of catalyst to 0·85 gm. with a thoroughput of phenol of 0·4 gm. per hour. For comparison, the experiments with phosphorus-promoted and the unpromoted molybdenum oxide catalyst were repeated, using the increased weight of catalyst. At 350° C. the conversion with unpromoted molybdenum oxide was 28·3 per cent. The results obtained over a range of temperature of 280°-350° C. with phosphorus, chromium and copper-promoted catalysts are shown in Fig. 3, together with a series of results obtained over a slightly more extended range of temperatures for a supported catalyst. This catalyst was similar to that used at the Fuel Research Station in the technical high-pressure hydrogenation process,[8] and was prepared by impregnating alumina gel with ammonium molybdate so that the catalyst contained 25 per cent. by weight of ammonium molybdate. In order to maintain standard conditions of preparation of the catalysts used in these experiments, the "unpreheated" catalyst [8] was used, *i.e.* the process of ignition in air at 500° C. which is carried out in preparing the catalyst for the technical process, was omitted. Experiments showed that this ignition, while it enhanced the activity of the catalyst for high-pressure hydrogenation, had very little effect on the activity for the reduction of phenol at atmospheric pressure, as carried out in these experiments.

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[7] *Amer. Chem. J.*, 1884, **5**, 391.

The chromium and copper-promoted catalysts were prepared from compounds of the second group, *i.e.* with six molybdenum atoms to each promoted atom. An analogous nickel compound was also prepared, but the catalyst thus obtained had an extremely variable activity, so the results are not given in detail here; in general, the results for the nickel-promoted catalyst were similar to those for the copper-promoted catalyst.

The activity-temperature curve for each catalyst was obtained with a single batch of catalyst without revivification, and it was found that during the series of experiments a slight deterioration of the catalyst took place. The catalyst could be restored to its initial activity by heating in hydrogen, the deterioration was therefore presumably due to the deposition on the catalyst surface of high-boiling products formed during the reaction. This deterioration is responsible for the slight spread of the experimental results shown in the curves, since on repeating a determination at any given temperature later in a series, a somewhat lower conversion was obtained.

From a comparison of the results both with unpromoted molybdenum oxide and the phosphorus-promoted catalyst, at the two different weights of catalyst, *i.e.* with different throughputs per gm. catalyst, it is clear that the conversion of phenol does not increase so rapidly as would be expected with the increase in time of contact. Thus the kinetics of this reaction are not as simple as indicated by equation (1), and therefore any values of the activation energy must be treated with some reserve. Calculations of the heat of activation have been made for several catalysts, and it was found that there was surprisingly little variation, all the values obtained being about 25,000 calories. This point will be discussed later.

Some experiments were also carried out with copper-promoted catalysts containing varying proportions of copper to molybdenum. Following the principle of preparing promoted catalysts if possible from chemical compounds rather than from physical mixtures, two catalysts with one copper atom to one and two molybdenum atoms respectively, were prepared[9] from the compounds $Cu\,MoO_4 . 2NH_3 . H_2O$, and $(NH_4)_2\,Cu(MoO_4)_2\,2NH_3$. A catalyst containing four molybdenum atoms to each copper atom was prepared by mixing in the requisite proportions, solutions of ammonium molybdate and copper nitrate and evaporating to dryness. The results obtained at 350° C. are given below, using 0·85 gm. catalyst.

TABLE II.

No. of Mo atoms per Cu atom .			6 (from Fig. 3)
Per cent. conversion of phenol	56·0	18·0	88·0

It will be seen that the catalyst obtained from the heteropoly-compound containing six molybdenum atoms to each copper atom is easily the most active, and so a more complete investigation of the other catalysts was not attempted.

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[8] King and Cawley, *Fuel Research Tech. Paper* (1935), No. 41. 4.

[9] Briggs, *J. Chem. Soc.*, 1904, 85, 672.

Determination of Surface Areas.

Since the activity of any given catalyst must be controlled both by the specific activity of the surface, and the total area of the catalyst, it was decided to make some measurements of the respective surface areas of the catalysts employed above. It is well known that the actual quantitative determination of the area of any adsorbent surface is difficult, since it depends on, among other factors, the accessibility of the surface to the substance used to measure the area, but it was felt that some estimate of the relative values for these catalysts might be obtained by determining their adsorptive capacities for a gas, such as carbon dioxide, the adsorption of which would be expected to be mainly of the Van der Waals type, under given conditions of temperature and pressure.

Accordingly, determinations were made of the volume of carbon dioxide adsorbed by the catalysts at 0° C. and atmospheric pressure. The apparatus consisted of a small bulb, containing the catalyst, immersed in melting ice in a Dewar flask, and connected to (*a*) a pumping system consisting of a mercury diffusion pump, backed by a Cenco " Hyvac " oil pump, (*b*) a McLeod gauge, and (*c*) a calibrated gas burette, which served both as the burette for measuring the volume of gas admitted and as the pressure manometer. The total volume of the adsorption apparatus, exclusive of the gas burette (and the pumping system and McLeod gauge, which were cut off from the adsorption apparatus proper except when evacuating) was 7·50 c.c., so that the adsorption capacity of catalysts with low surface areas could be evaluated with fair accuracy. Before the determination of the adsorptive capacity was carried out, the catalyst (which had been previously heated in hydrogen at 480° C.) was heated in vacuo at 480° C. for two hours. The results were obtained on Table III.

TABLE III.

Promoter.	Ratio: $\frac{\text{No. of Mo Atoms}}{\text{No. of Promoter Atoms}}$	Adsorption (c c. CO_2 per gm. Catalyst).
P . .	12	4·7
Cu . .	6	2·5
Cu . .	4	0·3
Cu . .	2	0·2
Cu . .	1	1·1
Cr . .	6	2·8
Th . .	12	1·55
Sn . .	12	ca 2·5
Unpromoted MoO_2 .	—	0·3
MoO_2 supported on alumina gel	—	9·7

An approximate value only is given for the tin catalyst, since it was found impossible to get a constant result for this catalyst.

It is clear, however, that neglecting minor differences, the catalysts can be divided into two main classes.

(*a*) Those with adsorptive capacitities about 0·3, including the unpromoted molybdenum dioxide catalyst, and two of the copper promoted catalysts; and

(*b*) Those with areas of 1·2-5, which include those active in the hydrogenation of phenol, and in addition the tin (which through its value is somewhat erratic undoubtedly had a fairly high adsorptive capacity) and thorium-promoted catalysts, which in spite of having a much larger apparent area than the unpromoted molybdenum oxide catalyst, are less efficient catalytically. The alumina-gel supported catalyst has by far the greatest surface, this in view of its comparatively low activity, suggests that although the method of preparation of this catalyst is designed to cover the alumina gel surface completely with molybdenum oxide, this has not been realised, and the molybdenum oxide is concentrated on certain portions only of the surface.

X-ray Examination of Catalysts.

As stated in the earlier part of this paper, X-ray examinations of the sulphide catalyst were made before and after heating, and similar examinations have been made of the oxide catalysts, in all cases after they had been subjected to the normal treatment of six hours heating in hydrogen at 480° C. The catalysts were mounted on fine glass fibres, and powder photographs taken using the copper Kα line (wave-length 1·54 Å.).

The results obtained can be summarised briefly as follows :—

(1) The phosphorus-promoted catalyst has an extremely micro-crystalline structure, giving an X-ray diagram consisting only of a diffuse halo (d = 2·4 Å.), so that its structure cannot be identified. The silica-promoted catalyst has a somewhat better developed crystalline structure, and the thorium catalyst is even more crystalline. The main lines of the X-ray diagrams in both cases correspond to those of molybdenum dioxide.

(2) The X-ray diagrams for the catalysts prepared from the heteropoly compounds of the second group (*i.e.* Cu, Cr and Ni—promoted catalysts) show well defined crystalline structures. The X-ray diagrams for these catalysts also corresponded within experimental error, both in spacings and intensities, to that for the molybdenum dioxide catalyst prepared from ammonium molybdate. A representative selection of the spacings (d) and the intensities of the lines of this diagram are given below, together with the data calculated for molybdenum dioxide.[10] The intensities were calculated, using the appropriate formula,[11] the parameter u in the structure factor [10] being taken as 0·3. Absorption effects were ignored; they would tend to reduce the intensity of the reflections for the planes with the larger spacings.

TABLE IV.

(Obs.).		(Calc.).		
d(Å).	Intensity	d(Å).	Intensity	
3·43	vs	3·44	10	(110)
2·45	vs	2·43 2·42	7·6	(200) (011)
2·14	w	2·17 2·165	0·5	(210) (111)
1·73	vs	1·72 1·715	6·6	(220) (211)
1·54	w	1·54	1·4	(310)

With the possible exception of the copper-promoted catalyst, it has not been possible to identify lines due to the promoters, but these lines would only be faint, and on the other hand, it is possible that the absence of the lines is due to the formation of solid solutions of the promoter in the molybdenum dioxide, the consequent distortion of the lattice being within the experimental error of the determination of film spacings.

(3) With the series of copper-promoted catalysts containing different proportions of copper, the X-ray diagrams are similar in that the main structure is that of molybdenum dioxide, but as the proportion of copper is increased new lines appear, the spacings of which agree with those calculated for copper.

(4) Samples of the phosphorus, chromium and silicon promoted catalysts were re-sintered in hydrogen at 700° C. and their X-ray diagrams taken. They show in each case that the molybdenum dioxide had been completely reduced to molybdenum.

The diagrams show also that the phosphorus and silicon-promoted catalysts had become much more crystalline in character as a result of the resintering process.

(5) The alumina gel supported catalyst gave an X-ray diagram exactly similar to that of pure molybdenum dioxide, the support, as would be

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[10] Wyckoff, *The Structure of Crystals*, p. 238;

[11] *International Tables for determination of Crystal Structure.*

expected, showing no crystalline structure, while the molybdenum dioxide was completely crystalline

Discussion.

A review of the data on catalytic activities and the values of the adsorptive capacities shows that a large surface area is necessary for a highly active catalyst. In the case of the phosphorus promoted catalyst (and to a lesser extent the silicon-promoted catalyst) the molybdenum dioxide is maintained in a nearly colloidal or amorphous state by the presence of the promoter atom, which furthermore confers a high degree of stability on this finely divided state, since it is only destroyed under conditions which lead to the complete reduction of the molybdenum dioxide to molybdenum.

On the other hand, the copper, chromium and nickel-promoted catalysts, have a well-developed crystalline structure, the original heteropoly compounds from which they are prepared being themselves crystalline. Nevertheless they are active catalysts, and have large surface areas, and it must be assumed that in the preparation of the catalysts by the decomposition of the crystalline heteropoly compound, the crystals develop a large internal area, and are not easily recrystallised to a denser form with lower surface area. Since the unpromoted catalyst is prepared in a similar way, by the decomposition of crystalline ammonium molybdate, the lower surface area and catalytic activity must be accounted for by the fact that any large internal area formed in this case is more easily destroyed on heating, by recrystallisation.

It must be noted, however, that while a large surface area is necessary in order to obtain a highly active catalyst it is possible to effect an increase in the total specific surface of the catalyst without increasing the catalytic activity. There are two promoted catalysts with fairly high surface areas, where the catalytic activity has been depressed by the addition of the " promoter," *i.e.* the tin and thorium-promoted catalysts.

The X-ray diagrams shows that (except in the case of phosphorus, where the catalyst structure cannot be identified) the main structure of all the catalysts is that of molybdenum dioxide itself. In the series of copper-promoted catalysts, as the copper content increases new lines appear, the spacings of which agree with those calculated for copper. These results are not in agreement with the observations made in the technical literature on the use of heteropoly-compounds as hydrogenation catalysts,[12] where it is stated that " care is taken that the said grouping " (*i.e.* that of the heteropoly-acid) " is not destroyed," whereas the results in this paper show that active catalysts can be obtained with systems where no trace of the original heteropoly-acid grouping is left--further, from the observations made in this work, it is doubtful whether such grouping could survive the conditions of hydrogenation experiments.

It has been shown earlier that the kinetics of the catalytic reduction of phenol are not as simple as that represented by equation (1). Further study of the reaction is necessary to elucidate it completely, but these experiments suggest that a possible explanation of the abnormalities observed is that some inhibition of the reaction by the products takes place (compare Aicher, Myddleton and Walker).[13] It has been shown also that there are no striking differences in the apparent energy of activation for the different catalysts, this may also be a consequence of the more complex nature of the reaction, and might be due to the fact that the energy of activation is determined by a process, such as the evaporation of the products from the catalyst surface, which has the same or similar energy for all the catalysts.

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[12] *Brit. Pat.* 371, 833.

[13] *J.S.C.I.*, 1935, 54, 313T.

Recent work by Griffith [14] has indicated that in the preparation of promoted catalysts by admixture of the catalyst and promoter, the concentration of the latter has a critical value, which may be similar for different promoters for the same reaction, but which varies according to the reaction used. Unfortunately, it is not possible to make a complete comparison of the catalyst-promoter ratios with those used in this work. And, on the other hand, while the preparation of the catalyst from the heteropoly-compound of molybdenum and the promoting atom of necessity does not permit of variation in the composition of the catalyst in order to prepare one of the critical composition, it has been shown above to be an extremely efficient method of promotion.

Summary.

1. Under the ordinary conditions of hydrogenation experiments molybdenum trisulphide is converted to the disulphide, and also becomes more crystalline in character with a consequent loss in catalytic activity.

2. Attempts were made to inhibit the sintering by the addition of promoters, using the hydrogenation of phenol to benzene as a measure of the activity of the catalyst. It was found that ammonium phosphomolybdate was a good promoter, and later, that it gave a highly active catalyst. A series of experiments are then described using catalysts prepared from a series of heteropoly compounds of molybdenum. It is shown that phosphorus, silicon, copper, nickel and chromium enhance the activity of the catalyst, tin and thorium depress it.

3. Determinations of the adsorptive capacities of the catalysts for Co_2 have been made. They show that while a high surface area is essential for an active catalyst, tin and thorium increase the area of the catalyst, but depress the activity.

4. X-ray diagrams have been obtained of the catalysts. The catalysts have the structure of molybdenum dioxide. In the phosphorus promoted catalyst the effect of the promoter is to maintain a micro-crystalline structure of the catalyst; the other catalysts have a well-developed crystalline structure.

The writer, who is a member of the research staff of the Department of Scientific and Industrial Research, carried out this work in the Department of Colloid Science, Cambridge, under the direction of Professor E. K. Rideal.

The author's thanks are due to Professor Rideal and to Dr. J. K. Roberts for their interest and advice, and to Mr. J. D. Bernal and Mr. A. G. Ward for facilities and help in carrying out the X-ray photography and analysis.

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[14] Griffith and Hill, *Proc. Roy. Soc. A*, 1935, 148, 193; Griffith, *Nature*, 1936, 137, 538; Griffith, *Trans. Faraday Soc.*, 1937, 33, 405.

THE EFFECT OF UNI-UNIVALENT ELECTROLYTES UPON THE INTERFACIAL TENSION BETWEEN NORMAL-HEXANE AND WATER.

By Arthur Wallace Evans.

(*Communicated by* W. C. M. Lewis.)

Received 13th April, 1937.

The effects produced by the presence of simple salts upon the free surface tension of water are well known. In general this tension is raised, although, as very recent work has shown (in the limited number of cases so far investigated)[1] a slight initial decrease occurs prior to a well-marked rise. On the other hand the effect of such salts on the interfacial tension between a saturated hydrocarbon, and water is a matter of some uncertainty. Thus W. C. M. Lewis[2] believed he had obtained a fall whilst M. Kidokoro[3] has observed a rise on the addition of such salts to the aqueous phase.

In view of the importance to colloid chemistry of the point in question, *i.e.*, whether positive or negative adsorption of the ions of the added electrolyte occurs at an oil-water interface, a further investigation of the point was considered to be of interest.

Experimental Method.

The measurements described in this paper were carried out using a drop-volume apparatus, similar to that described by D. J. Dedrick and M. H. Hanson.[4] The dropping tip was made of quartz, the rest of the apparatus including the needle valve, being made of Pyrex glass. The whole apparatus was mounted rigidly in an air-thermostat, by means of which the temperature of the apparatus and its contents was maintained at 25·0 ± 0·15° C. The rate of formation of the drops was controlled by the vertical movement of a needle valve which was operated from outside the thermostat.

In all these measurements, the aqueous phase, being the denser, was allowed to drop into the *n*-hexane, which was placed in a 100 c.c. weighing bottle into which the quartz tip dipped. The two phases were kept in the thermostat for twelve hours before measurements were performed, in order to ensure that they had reached the temperature of the thermostat.

The diameter of the quartz tip was measured by means of a cathetometer, the mean of eight values being taken. The volume of the pipette between two marks on the stem of the pipette, above and below the bulb, and also the area of cross-section of the stem in the neighbourhood of these two marks were determined. This was done by performing three experiments using distilled water and with the weighing bottle empty. The amount of water which had run out of the pipette was weighed in each case. Each experiment gave an equation connecting the three required quantities; the three equations were then solved. The whole procedure was repeated twice, and three values for each of the required quantities obtained.

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[1] G. Jones and W. A. Ray, *J. Amer. Chem. Soc.*, 1937, **59**, 187.

[2] W. C. M. Lewis, *Phil. Mag.*, 1909, **6**, 17, 466.

[3] M. Kidokoro, *Chem. Soc. Japan Bull.*, 1932, **7**, 280.

[4] D. J. Dedrick and M. H. Hanson, *J. Physic. Chem.*, 1933, **37**, 1215.

The vertical height of the meniscus above or below the mark on the stem at the start, and also at the end of a measurement, was measured by means of a vertical cathetometer. These heights were measured to 0·001 cms.

The values obtained for the dimensions of the apparatus were as follows:—

Radius of the quartz tip = 0·408 cms.
Volume of the pipette = 18·25 mls.
Cross-section of stem at:—
(*a*) Upper mark = 0·59 squ. cms.
(*b*) Lower mark = 0·27 squ. cms.

The results were calculated using the following equation:—

$$\gamma = \frac{V \times (d_2 - d_1) \times g}{2\pi R \times \psi}$$

where V = volume of each drop, d_1 and d_2 are the densities of the two phases, R is the radius of the dropping tip, g is the gravitational constant, and ψ is the fraction of the pendant drop which actually falls. The values of ψ were obtained from the data of Harkins and Brown.[5] A large graph was plotted of ψ against $R/V^{\frac{1}{3}}$ using their data. The value of $R/V^{\frac{1}{3}}$ was calculated for each measurement and the corresponding value of ψ was read off from this graph.

The *n*-hexane used was the B.D.H. product, which was specially pure for spectroscopic work. In practice this material, however, was found to vary from batch to batch as tested by its capillary behaviour; a range of 0·3 dynes/cms. being found in the values of the interfacial tension against water for different batches. The purity of the *n*-hexane was tested spectroscopically and was found to exhibit no selective absorption over the range of wave-length 2100-7000 Å., using a quartz cell 2 cms. thick.* This demonstrated that the *n*-hexane was free from unsaturated compounds, halogen compounds, alcohols, phenols, ethers, etc.

The discrepancy between the batches was therefore ascribed to the presence of small quantities of neighbouring paraffins in the *n*-hexane. A number of batches were therefore thoroughly mixed in order that all the measurements could be performed using the same material. The presence of these neighbouring paraffins does not affect the theoretical value of the work. The density of the *n*-hexane was determined at 25·0° C., the value obtained being 0·6687 grs./mls., this being correct to four figures.

The salts used were dissolved in freshly distilled water; the densities of the resulting solutions being obtained from the International Critical

TABLE I.

Experiment.	V.	$R/V^{1/3}$.	ψ.	Interfacial Tension.
(1)	0·2421 mls.	0·6546	0·6160	49·56 dynes/cms.
(2)	0·2424 ,,	0·6545	0·6160	49·62 ,, ,,
(3)	0·2427 ,,	0·6542	0·6160	49·67 ,, ,,
				Average value = 49·62 *dynes/cms.*

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[5] Harkins and Brown, *J. Amer. Chem. Soc.*, 1919, 41, 499.

* The writer is indebted to Dr. R. A. Morton for this examination of the hydrocarbon.

TABLE II.

Concentration of Electrolyte (moles/litre).	Interfacial Tension (dynes/cms.).				
	NaCl.	KCl.	RbCl.	CsCl.	KNO$_3$.
0·00	49·53	49·53	49·53	49·53	49·53
0·01	49·65	49·64	49·53	49·62	49·58
0·02	49·70	49·66	49·52	49·62	49·62
0·03	—	—	—	49·63	—
0·05	49·67	49·72	49·67	49·66	49·69
0·07	—	—	49·69	49·71	—
0·10	49·69	49·69	49·77	—	49·69
0·20	—	—	—	—	49·75
0·30	50·13	49·94	—	—	—
0·40	—	—	—	—	49·88
0·50	50·47	50·21	—	—	—
0·70	50·64	—	—	—	49·95

Tables, except in the case of the potassium thiocyanate solutions where no such data were available.

TABLE III.

Concentration of Electrolyte (moles/litre).	Interfacial Tension (dynes/cms.).		
	LiCl.	NaOH.	KCNS.
0·00	49·53	49·53	49·53
0·01	49·49	49·44	49·62
0·02	49·43	49·51	49·57
0·05	49·49	49·50	49·41
0·10	49·59		49·31
0·20	—		49·23
0·30	49·86	49·93	—
0·50	50·18	—	—
0·70	50·20	50·66	—
0·93	50·51		—

In order to indicate the degree of reproducibility in the measurements the data obtained for a single typical case, namely 0·02 molar potassium nitrate are given in Table I.

The results are given in Tables II. and III. and are in each case the mean of three or four measurements, and are accurate to ± 0·10 dynes/cms.

Discussion.

The results in Table II., *i.e.*, for sodium, potassium rubidium, cæsium chlorides and potassium nitrate, exhibit a marked similarity to those obtained by Heydweiller[6] and Schwenker[7] for the surface tensions of aqueous solutions of the alkali metal chlorides. The two cases differ however in that the increments in the interfacial tension for the *n*-hexane/water interface are smaller than the increments at the air/water interface. For concentrations up to 0·10 molar, the values obtained for these salts lie on the same curve, within the experimental error. From these results it appears that the different alkali metal ions, and also the chloride and nitrate ions, behave in an identical manner. The differences in the size and nature of the ions have no observable effect on the interfacial tension at low concentrations. The effect of these ions is therefore to be ascribed in the first instance to the electrostatic charges which they possess.

Various theories have been proposed to explain the effect of simple salts on the surface tension of water, the most satisfactory being that due to Wagner,[8] and its simplified version due to Onsager and Samaras.[9] This theory is based upon the repulsion between an ion and its electrostatic image in the non-aqueous phase. The potential of an ion is then calculated in terms of its distance from the interface, allowance being made for the screening effect of its ionic atmosphere. Then by application of the Maxwell-Boltzmann equation the concentration of the ions at any particular distance from the interface is obtained. Integration of this expression gave the total negative adsorption of the ions. This value for the negative adsorption was then substituted in the Gibbs' adsorption isotherm, and an expression connecting the concentration of the ions in the bulk of the solution and the increment in the interfacial tension was obtained. The Onsager-Samaras equation gives the correct form of the curve but is lower than the experimental curve both in the case of the surface tension of aqueous solutions of salts and in the case of their interfacial tension against n-hexane. Onsager and Samaras suggest that the cause of this discrepancy (which implies additional repulsive forces between the ions and the interface) may be due to quadruple and second order dipole effects.

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[6] Heydweiller, *Ann. Physik.*, 1910, 4, 33, 145.

[7] Schwenker, *ibid.*, 1931, 11, 525.

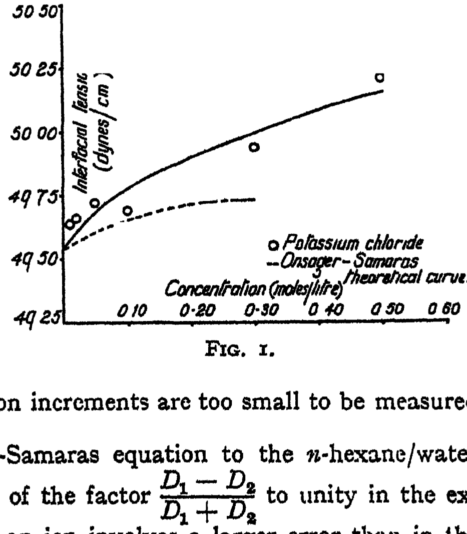

FIG. 1.

Fig. 1 shows the experimental curve for potassium chloride and the theoretical curve of Onsager and Samaras. It should be remembered that this theory suffers from the same limitations as the Debye-Hückel theory of strong electrolytes, and can only be expected to apply at all accurately to very dilute solutions. At such concentrations the interfacial tension increments are too small to be measured with accuracy.

In applying the Onsager-Samaras equation to the n-hexane/water interface, the approximation of the factor $\frac{D_1 - D_2}{D_1 + D_2}$ to unity in the expression for the potential of an ion involves a larger error than in the case of the air/water interface. D_1 and D_2 are the dielectric constants of the aqueous and non-aqueous phases respectively. In the case of the air/water interface, the approximation produces an error of 2·3 per cent. in the expression for the potential of an ion, while in the case of the n-hexane/water interface the error is 4·5 per cent. If the approximation is not made then the expression for the potential of a particular ion will be greater when the non-aqueous phase is air than when it is n-hexane. Therefore accurate application of the "electrostatic image theory" leads to the conclusion that the increments of interfacial tension produced by the added electrolyte should be less in the case of the n-hexane/water interface than in that of the air/water interface. As mentioned above this conclusion is borne out by experiment. The rival theories due to Ariyama[10] and Oka[11] do not lead to this result. According to these theories the nature of the non-aqueous phase is immaterial, provided it has no solvent action with respect to the added electrolyte.

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[8] Wagner, *Physik. Z.*, 1924, **25**, 474.

[9] Onsager and Samaras, *J. Chem. Physics*, 1934, **2**, 528.

The theoretical treatment of Onsager and Samaras leads to the conclusion that at the interface, there exists a layer of pure water in contact with the non-aqueous phase. Electrophoretic measurements, on air bubbles by McTaggart[12] and on emulsions of hydrocarbon oils by Powis[13] show that the interface must possess a resultant negative charge, even when the aqueous phase is pure water. The presence of this charge is ascribed to a layer of primarily adsorbed hydroxyl ions which are balanced by rigid and diffuse layers of hydrogen ions. This double layer can be regarded as a layer of orientated water molecules, in which the hydroxyl and hydrogen ions are only loosely held together; some of the hydrogen ions being so loosely held as to form the diffuse layer. The presence of a layer of primarily adsorbed hydroxyl ions leads one to the conclusion that the experimental value for the interfacial tension between *n*-hexane and water, and also for the surface tension of water, are depressed values as compared with the values which would obtain in the entire absence of an electrical " double layer." This lowering is possibly due to the repulsive forces between the adsorbed hydroxyl ions in the plane of the interface.

It is clear that the presence of the double layer at the interface makes the treatment of Onsager and Samaras inadequate. Consider an ion of the added electrolyte situated in the diffuse layer. If the ion is positively charged, then in addition to the repulsive force between it and its electrostatic image in the non-aqueous phase, there will be an attractive force between the ion and the rigid double layer, due to the resultant negative charge of the latter. In the case of an ion negatively charged, similarly situated, the repulsive force between the ion and its electrostatic image will be augmented by the repulsion between the ion and the rigid double layer. Since in the diffuse region there are more positive than negative ions, the presence of the double layer will tend to reduce the repulsion between the ions as a whole and the interface. This should tend to reduce the increments in the interfacial tension. The double layer, however, has another effect. Consider a positively charged ion situated in the diffuse layer. Owing to the excess of positively charged ions throughout this region, the ionic atmosphere of negatively charged ions surrounding the ion will be weaker than for a similar ion situated in the bulk of the solution. Consequently for positive ions, so situated, the screening effect due to their ionic atmospheres will be less, and therefore the repulsive force between the ion and its electrostatic image will be greater than the calculated value of Onsager. In the case of negative ions situated in the diffuse region, the ionic atmospheres of positive ions will be stronger than for similar ions in the bulk of the solution. Consequently the repulsive forces between negative ions in the diffuse layer and their electrostatic images in the non-aqueous phase will be reduced. Since there are more positive than negative ions in the diffuse layer, it is clear that this effect will tend to cause the increments in the interfacial tension to be greater than those predicted by the Onsager-Samaras equation.

[10] Ariyama, *Bull. Chem. Soc. Japan*, 1936, 2, 10, 687.

[11] Oka, *Proc. Phys. Math. Soc. Japan*, 1932, 14, 233.

[12] McTaggart, *Phil. Mag.*, 1914, 27, 297.

[13] Powis, *Z. physik. Chem.*, 1915, 89, 91.

The electrostatic double layer, therefore, complicates the Onsager-Samaras theory in two ways :—

(1) The electrostatic forces between the rigid double layer and the ions in the diffuse layer will tend to reduce the interfacial tension increments.

(2) The difference between the ionic environments of ions in the diffuse layer and of those in the bulk of the solution should tend to cause greater increments of interfacial tension.

If the latter effect is the greatest, then the discrepancy between the theoretical and experimental curves can be attributed to neglect of the existence of the electrostatic double layer at the interface.

In the results considered so far, the effects of the added electrolytes have been explained by attributing them to the ions produced in solution. The ions were treated solely as electrostatic charges. The results given in Table III., however, require the assumption of specific "chemical" forces to explain them.

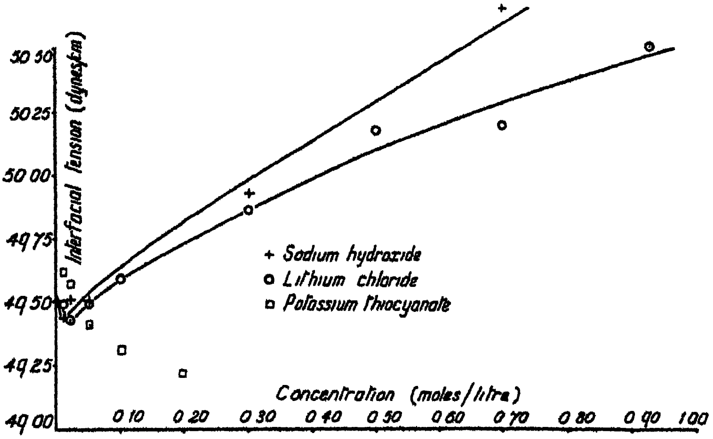

FIG. 2.

These results are illustrated in Fig. 2. The sodium hydroxide curve exhibits a small minimum at low concentrations. This minimum is attributed to the hydroxyl ion, since there is no reason to believe that the sodium ion will behave differently in the case of sodium hydroxide from what it does in the case of sodium chloride. If the layer of primarily adsorbed hydroxyl ions at the *n*-hexane/water interface is not quite complete, then if the bulk concentration of hydroxyl ions is increased, one would expect more hydroxyl ions to be adsorbed, until the adsorbed layer was complete. It is therefore suggested that the observed initial lowering of the interfacial tension is due to primary adsorption of hydroxyl ions. Once the layer is complete, the caustic soda behaves in the same way as sodium chloride.

The lithium chloride curve also exhibits a small minimum at low concentrations. Lithium chloride is well known for its tendency to form co-valent molecules which are soluble in certain organic solvents. Even in dilute solutions these molecules will be present, though only in small concentration. These co-valent molecules will be attracted to the interface and adsorbed, thus causing a lowering of the interfacial tension. Once that portion of the interface not already covered by the hydroxyl ions, is covered by the lithium chloride molecules, the curve behaves in a similar manner to the other alkali metal chlorides.

The potassium thiocyanate curve indicates that positive adsorption is occurring. This must be due to the thiocyanate ion which must be held at the *n*-hexane surface by specific chemical forces.

Summary.

(1) Experimental results are given showing the effect of the alkali metal chlorides, of potassium nitrate, of potassium thiocyanate, and of sodium hydroxide on the interfacial tension between *n*-hexane and water at 25·0° C.

(2) Comparison of the results for the alkali metal chlorides with the corresponding surface tension results, supports the Onsager-Samaras theory as opposed to the theories of Ariyama and Oka.

(3) The effect of the existence of the electric double layer at the interface on the theoretical treatment of Onsager and Samaras is discussed, and a suggested explanation of the discrepancy between the theory and the experimental results is given.

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THE PHOTOREACTION OF HYDROGEN IODIDE AND METHYL IODIDE.

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It is always assumed that organic iodine compounds such as the alkyl iodides (RI) dissociate under the influence of light into R and I (perhaps $^2P_{\frac{1}{2}}$). Their absorption spectra are continuous,[1, 2] and there is an absence of fluorescence. Attempts to locate the long-wave limit of the absorption and relate it to the energy of binding of the C-I linkage have not been wholly successful.[2, 3, 4] The earlier investigators were content to say that because iodine was liberated under the influence of light, the excitation was in the C-I bond, and dissociation followed the repulsion state set up between the nuclei. The case was regarded as similar to the hydrogen iodide dissociation. Nevertheless, photochemical experiments carried out with these iodides have not always verified in any striking manner the predictions made from the absorption spectra.

The quantum yield in the simple decomposition process should be at least unity if $RI + h\nu = R + I$ is the change taking place, and the radical R is used up in forming the hydrocarbon RR (probably a three-body or wall reaction). The quantum yield will be greater than unity if secondary reactions such as $R + RI = RR + I$ take place, and less than unity if

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[1] Herzberg and Scheibe, *Z. physik. Chem.*, *B*, 1930, 7, 390.
[2] Iredale and Mills, *Proc. Roy. Soc.*, *A*, 1931, 133, 430.
[3] Iredale and Wallace, *Phil. Mag.*, 1929.
[4] Iredale and Stobo, *Z. physik. Chem.*, *B*, 1933, 20, 340.

the life of the radical is long enough for such a recombination as $R+I=RI$ or such a reaction as $CH_3 + I_2 = CH_3I + I$ to occur to any appreciable extent.

Particular mention must be made here of the work of Chadwell and Titani,[5] who studied the reaction between H atoms and CH_3I. They found that CH_4, C_2H_6, HI and I_2 were the main products. The reactions are:

$$CH_3I + H = CH_3 + HI \tag{1}$$
$$HI + H = H_2 + I \tag{2}$$
$$CH_3 + HI = CH_4 + I \tag{3}$$
$$CH_3 + HI + H = CH_3I + H_2 \tag{4}$$
$$CH_3 + H = CH_4 \text{ (3 body)} \tag{5}$$
$$CH_3 + I = CH_3I \text{ (3 body)} \tag{6}$$
$$H + I = HI \text{ (3 body)} \tag{7}$$
$$I + I = I_2 \text{ (3 body)} \tag{8}$$
$$CH_3 + CH_3 = C_2H_6 \text{ (3 body)} \tag{9}$$

They do not consider the possibility of the reactions:

$$CH_3 + CH_3I = C_2H_6 + I \tag{10}$$
$$CH_3 + I_2 = CH_3I + I \tag{11}$$

But it would seem from their results that the two-body reaction (3) takes place more rapidly than the three-body reactions (4), (5), (6), (9) and also (10) and (11), which remove CH_3. Nevertheless, since ethane was produced in some quantity, reactions (9) and (10) cannot be considered to be of negligible importance. But it must be remembered that Chadwell and Titani's experiments were carried out with H atoms very much in excess of the halide present. Reactions (1) and (5) would be of relatively great frequency compared with those regenerating the halide.

Now, some of these reactions are involved in the photodecomposition of methyl iodide, if we assume that CH_3I dissociates into CH_3 and I; (6), (8), (9), (10) and (11) would seem to be. But ethane is not formed [6] to any great extent,[7] so that (9) and (10) are of rare occurrence. Their collision efficiency must be very small with (6) and (11). However, the small yield of ethane may have to be explained in some other way. Chadwell and Titani's results do not altogether fit in with the photochemical results.[7]

Moreover, since higher iodides are found in small quantities, reactions of the type:

$$CH_3 + CH_3I = CH_4 + CH_2I \tag{12}$$
$$CH_2I = CH_2 + I \tag{12a}$$
$$CH_2 + I_2 = CH_2I_2 \tag{13}$$

may take place to some extent.

Emschwiller [6] found methylene iodide in liquid CH_3I after irradiation, but he considers it is formed by the reaction:

$$CH_3{}^*I + CH_3I = CH_4 + CH_2I_2 \tag{14}$$

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[5] Chadwell and Titani, *J. Amer. Chem. Soc.*, 1933, **55**, 1363.

[6] Emschwiller, *Ann. Chimie*, 1932, **17**, 413.

[7] Spence and Wild, *Proc. Leeds Phil. Lit. Soc.*, 1936, **3**, 141. These investigators obtain some ethane on irradiation of CH_3I, but only small amounts. From their figures, 1000 absorbed quanta produced 32 molecules of methane, 16 atoms (8 molecules) of free iodine and some polyiodide (CH_3I_3 ?) all from 60 decomposed molecules of CH_3I. This leaves only 3 molecules of ethane to be accounted for, which is relatively small compared with the methane.

Those who have studied the absorption spectrum of CH_3I do not think that the excited molecule ($CH_3{}^*I$) is formed, but it is possible that in the liquid state the molecule is unable to dissociate fast enough previous to a collision with another molecule, so that the Franck-Rabinowitsch[8] mechanism may operate in this case, and Emschwiller's equation may be correct.

Very astonishing is the fact that the addition of hydrogen to the photochemically decomposing CH_3I has no influence on the quantum yield.[7, 9] The reaction:

$$CH_3 + H_2 = CH_4 + H \quad . \quad . \quad . \quad . \quad (15)$$

in removing the CH_3 and forming an H atom, must inevitably increase the quantum yield. But the low collision efficiency of (15) compared with even such three-body reactions as (6), is thought sufficient to account for this.

Now Patat[10] has recently calculated the activation energy for (15) to be 9000 calories. He also thinks that (15) is by no means improbable in the CH_3I case, although the photochemical results do not uphold the assumption. Patat has endeavoured to explain the results of West's experiments[11] on the *orthopara* hydrogen interconversion, which West thinks is accomplished by the paramagnetic radical CH_3 from CH_3I. West assumed a stationary concentration of CH_3, which Patat calculates is too small, and instead, Patat arrives at the necessary change through the assumption of reaction (15). West by no means excludes from consideration the possibility of the existence of a paramagnetic excited molecule ($CH_3{}^*I$) induced by the light, but prefers to assume (as, indeed, one would normally conclude from the continuous nature of the absorption spectrum) the existence of the CH_3 radical.

If the CH_3 radical exists it should be capable of reaction if not with H_2, at least with some other molecule, where the collision efficiency is greater. The reaction with metallic films would be difficult to carry out, owing to the possibility of the simultaneous reaction of the film with I atoms. We thought that the reaction $CH_3 + HI = CH_4 + I$ would fulfil the purpose.

The photochemical behaviour of CH_3I — HI mixtures would seem to be straightforward enough. The primary changes:

$$CH_3I + h\nu = CH_3 + I$$
$$HI + h\nu = H + I$$

would be followed by reactions (1) to (11). Owing to the high collision efficiencies of (1), (2) and (3), we would expect a quantum yield of two for the photodecomposition, unless the concentration of HI were low, and reactions (6), (11), etc., became pronounced. We are able to draw these conclusions from the results of Chadwell and Titani.[5] On the other hand, if the CH_3I excited by light, instead of dissociating, rearranges its internal energy in some way to give another excited (perhaps metastable) state ($CH_3{}^*I$), we would have to consider the reaction

$$CH_3{}^*I + HI = CH_4 + I_2$$

comparable with the thermal reaction.[12] The quantum yield in this case would have a maximum value of 2, but this would progressively fall off as the concentration of HI was diminished, as the possibility of deactivation of the $CH_3{}^*I$ would become greater; otherwise it would be difficult to explain on the CH_3I^* hypothesis, the low quantum yield in the case of CH_3I alone.

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[8] Franck and Rabinowitsch, *Trans. Faraday Soc.*, 1934, **30**, 120.
[9] Bates and Spence, *J. Amer. Chem. Soc.*, 1931, **53**, 1689.
[10] Patat, *Z. physik. Chem.*, 1936, **32**, 274.
[11] West, *J. Amer. Chem. Soc.*, 1935, **57**, 1931.
[12] Ogg, *ibid.*, 1934, **56**, 526.

Experimental.

Hydrogen iodide was generated from pure, previously boiled 85 per cent. H_3PO_4 and pure KI in, the flask A, water, I_2, etc., were condensed in B with the aid of solid CO_2. The HI was condensed by liquid air in C, and distilled into D. A pure sample of CH_3I was distilled over from E into F. The vapours of HI and CH_3I were mixed in the chamber M, the whole of this system having approximately the same volume as the system including the quartz photochemical cell R. The mixing of the two vapours presented a slight difficulty owing to their slow interdiffusion. By applying inequalities of temperature to various portions of the bulb M, it was found possible to mix them adequately. CH_3I and HI do not react appreciably at room temperature, but a very slight reaction (probably a wall reaction) is inclined to take place when the vapours are left together for any length of time. In determining, therefore, the iodine formed from the photo-decomposition, we condensed out with liquid air the products in L_2 as well as in L_1, and estimated the total iodine in both cases; the small amount in L_2, due to the thermal effect, being subtracted from the amount in L_1. $N/400$ $Na_2S_2O_3$ was used to titrate the iodine, and CO_2 was passed into the solution containing the I_2 and KI during the titration. We found that in the absence of CO_2 or other inert gas, the rapidly evaporating HI tended to decompose on coming in contact with the air. The $N/400$ $Na_2S_2O_3$ was standardised against solutions of known iodine content.

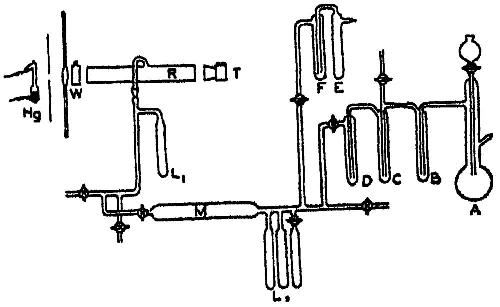

FIG. 1.

The photo-chemical set-up, calibrations, and details of measurements, etc., were not essentially different from those described elsewhere.[13] But we used the full light of the mercury arc, and had to arrive at a value for the "average quantum" by studying the decomposition of HI alone, and using Warburg's figure[14] ($\gamma = 2{\cdot}07$ for the region 2600-2700Å, where the most intense absorption lay). Since, in this region CH_3I and HI have almost identical absorption spectra,[1] the same long-wave absorption limits,[8],[15] and similar extinction coefficients[14] (that of CH_3I being slightly greater than that of HI), no great error was incurred through using polychromatic light and a mean value for the quantum. The absorption deflections taken during experiments indicate quite closely equivalent absorptions for CH_3I and HI in the 2600Å region. Actually, the wave-length of the quantum came out to be 2600Å, using Warburg's

TABLE I.

Pressure of HI.	γ.
42 mm.	2·30
80	1·92
127	(3·40)
153	2·25
160	2·35
220	2·30
238	2·10
282	2·10

Mean : 2·19

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[13] Gibson and Iredale, *Trans. Faraday Soc.*, 1936, 32, 571.
[14] Warburg, *Sitz,. Ber. Preuss. Akad. Wiss.*, 1918, 1, 300.
[15] Tingey and Gerke, *J. Amer. Chem. Soc.*, 1926, 48, 1838.

figure, although this was an average of a number of determinations. Continuing these measurements, and using the wave-length 2600Å, we finally arrived at $\gamma = 2 \cdot 19$, which is a little higher than Warburg's figure. Actually, Warburg's figure at 2800Å varies from 2·35 to 1·95. We obtained variations of the same order, as will be seen from Table I.

Variations outside this range were traced to too inadequate experimental conditions, which had to be rectified. Hydrogen iodide is not an easy substance to handle, outside the vacuum system. Minute traces of oxygen hasten its decomposition, and it is also capable of decomposing, even at low temperatures, on certain glass surfaces. It does not readily attack stop-cock lubricant, unless small amounts of air or oxygen are present, nor is this material affected by the iodine formed, as it has a negligible iodine value. In our experiments, we found that all the iodine could be withdrawn by liquid air.

We did not wish to obtain a very accurate value for the quantum yield, but only to find out how it changed with the composition of the HI-CH_3I mixtures, and only to be certain that the variations were outside the limits of possible experimental error. We were fortunate in discovering that there was scarcely any variation in the average quantum yield as we changed from pure HI to HI-CH_3I mixtures having as little as 40 per cent. of HI in their composition, but for mixtures having only 5-10 per cent. HI, the decrease in γ was considerable. The intermediate region of the curve where γ is changing fairly rapidly has been omitted, because we do not think that the order of accuracy of our experimental results could give us the form of the curve with sufficient exactness. Moreover, for the purposes of the present discussion, it is not necessary.

TABLE II.

Pressure of HI.	Pressure of CH_3I.	Percentage HI in Total Gaseous Mixture.	γ (Temp. 17°–20° C.).
187 mm.	194 mm.	49	(1·6)
175 ,,	25 ,,	88	1·9
100 ,,	100 ,,	50	2·4
100 ,,	100 ,,	50	2·0
100 ,,	100 ,,	50	2·3
90 ,,	98 ,,	48	1·89
88 ,,	88 ,,	50	1·98
80 ,,	120 ,,	40	2·1
71 ,,	73 ,,	49	2·3
46 ,,	58 ,,	44	2·04
20 ,,	180 ,,	10	0·8
12 ,,	190 ,,	6	0·6
10 ,,	190 ,,	5	1·1
0 ,,	190 ,,	0	<0·1

The amounts of iodine estimated in these experiments were of the order 10^{18}-10^{19} atoms.

Discussion.

The circumstance that we obtained a quantum yield of 2 even for mixtures of CH_3I and HI containing only 40 per cent. HI shows that there is a great probability of the long-lived radical CH_3 being formed, and that the collision efficiency of the reaction $CH_3 + HI = CH_4 + I$ is very high. For, if the electron excitation of the CH_3I molecule led finally to some condition of redistribution of the energy ($CH_3{}^*I$), the reaction $CH_3{}^*I + HI = CH_4 + I_2$ would have to be one of high collision efficiency, and to take place before deactivation of $CH_3{}^*I$ occurred. This deactivation would become more and more probable as the $CH_3{}^*I$ concentration was increased, so that the quantum yield would gradually fall off as the HI was replaced by CH_3I. However, the $CH_3{}^*I$ hypothesis would explain the fact that H_2 has no influence on the quantum yield in the case of CH_3I alone, as it is improbable that any reaction would take place between $CH_3{}^*I$ and H_2.

We may be able to obtain some information on this matter by working at higher temperatures, where the reaction $CH_3 + H_2 = CH_4 + H$ is more likely to take place.

The results of our investigation seem to rule out the possibility that the primary act of photodissociation of CH_3I is $CH_3I = CH_2 + HI$, although this is not impossible from energy considerations, even if the CH_2 radical were to remain with the C atom in the higher, tetravalent state. The reunion of CH_2 and HI would account for the low quantum yield, but the addition of HI to the CH_3I would not change the yield for that part of the photoreaction which is produced by the CH_3I light absorption. A maximum of unity would be obtained for the quantum yield where 50 per cent. of the light was absorbed by the HI.

Summary.

The quantum yield for I_2 produced has been investigated in the case of CH_3-HI mixtures.

This yield is ~ 2 for a considerable range of composition of these mixtures. Of the hypotheses advanced to account for the reactivity of the CH_3I after light absorption, the one involving dissociation into CH_3 and I seems at present to be the one which agrees best with our results.

Photodissociation of CH_3I into CH_2 and HI seems to be ruled out of consideration.

One of us (D. S.) is indebted to the University of Sydney for a Science Research Scholarship.

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THE GIBBS ADSORPTION EQUATION AND ADSORPTION ON SOLIDS.

BY D. H. BANGHAM.

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Evidence given in a recent series of papers[1] has pointed to a parallelism between the behaviour of certain adsorbed films on solids and the often better-understood effects at liquid-gas interfaces. The surface tensions and energies of solids being incapable of direct measurement, the influence on them of adsorbed films has attracted but little attention, in spite of the obvious bearing of such effects on problems of cohesion and adhesion. In this paper, an attempt is made to examine the implications, with respect to these variables, of the postulates which form the basis of the theory of chemisorption; the object in view being that of discriminating between those similarities in the properties of surface films which follow as a necessary consequence of the thermodynamic laws, and those which are indicative of real similarity of behaviour.

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[1] "The Swelling of Charcoal," *Proc. Roy. Soc., A*, Part (I.), 1930, **130**, 81; (II.), 1932, **138**, 162; (III.), 1934, **147**, 152; (IV.), 1934, **147**, 175.

Gibbs[2] points out that with solid, as opposed to liquid surfaces, the surface energy, representing work spent in forming unit area of new surface, cannot, in general, be equated to a *tension*, for the work spent in extending a surface by a process of *stretching* which brings no additional atoms into the interface may have quite a different value. This distinction has constantly to be borne in mind in connection with chemisorption.[3] A film containing only chemisorbed molecules between which no tangential repulsive forces are acting would clearly be without effect on the work of stretching, though it would reduce the surface energy. With a *physically* adsorbed film, on the other hand, in which the molecules have no fixed points of attachment, the effects on the two kinds of work would be equal; so far from being a thermodynamic abstraction, the surface energy lowering can then be identified as a surface "pressure," just as at liquid surfaces.

The Adsorption Equation of Gibbs.

The adsorption equation of Gibbs, applicable to the case where only one gas is present at the surface of a solid or liquid in which it is nearly insoluble,[4] becomes

$$\Gamma = -\left(\frac{\partial\sigma}{\partial\mu}\right)_T \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where Γ is the "surface concentration" of the adsorbed gas in moles per cm.^{2}, μ its chemical potential, T the absolute temperature, and σ the work required to form 1 cm.^{2} of new surface under the environmental conditions defined by T and μ. Harkins [5] points out that this equation automatically takes into account any electrical effects at the interface, since the interfacial energy is completely defined by the chemical potentials of the components of the system so long as no external potential difference is applied across the boundary.

For an adsorbate which is a perfect gas we can replace $\partial\mu$ by $RT\partial \log p$, p being the pressure; and if σ_0 is the value of σ for $p = 0$, that is, the work required to form 1 cm.^{2} of clean surface, we obtain, on integration,

$$\sigma_0 - \sigma = RT\int_0^p \Gamma d \log p \quad . \quad . \quad . \quad . \quad (2)$$

If we denote by F the surface energy lowering ($\sigma_0 - \sigma$), equations (1) and (2) then give us

$$\Gamma = (\partial F/\partial\mu)_T = RT(\partial F/\partial \log p)_T \quad . \quad . \quad . \quad (3)$$

$$F = RT\int_0^p \Gamma d \log p \quad . \quad . \quad . \quad . \quad (4)$$

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[2] *Collected Works*, 1928, 1, 315.

[3] For clarity it is assumed, in what follows, that *chemi*sorbed molecules have unrestricted freedom of tangential movement if the surface is that of a liquid, and no translational movement whatever if it is that of a solid. Strictly speaking, this sharp distinction is inadmissable, in view of the known quasi-regular structure of liquids—particularly in their surface layers—and the recognised possibility that atoms or molecules forming the external layers of crystals may have a certain freedom of migration.

[4] This condition ensures that the physical significance attaching to Γ shall not depend on the arbitrary choice of the geometrical surface, in terms of which it is defined, as one which will make the surface excess concentration of the non-volatile component vanish. *Vide* Guggenheim and Adam, *Proc. Roy. Soc., A*, 1933, 139, 218.

[5] *Colloid Symposium Monograph*, 1928, 6 (discussion).

The condition for a finite value of F is that the ratio Γ/p shall remain finite or at the worst integrable down to zero pressure.

Gibbs's treatment ascribes to the interface the properties of a single phase of continuously variable composition. Provided there is no lack of homogeneity in the film in directions parallel to the interface, this is fully justifiable, even though the latter may be complex in structure, comprising, perhaps, one or several layers of molecules superimposed on one that is chemisorbed. Rideal[6] points out, however, that the presence on an otherwise uniform substrate of regions of different concentrations, constituting two surface phases, would introduce the further condition for equilibrium that

$$\mu_1 = \mu_2 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

these being respective chemical potentials of the gas in the two phases. A degree of freedom thus being lost, at an arbitrarily fixed temperature the pressure would necessarily remain invariant until one of the phases has disappeared, the isotherm therefore having the stepped form of the broken-line graph in the figure. Fowler[7] has shown statistically how, given certain postulates, this type of isotherm may arise in a case of chemisorption; a necessary condition is that the heat of adsorption should increase with the degree of covering.

It is important to note that since equation (3) applies to each of the two surface phases considered separately, F can still be correctly evaluated with the aid of (4). This is true because when there is equilibrium we have also

$$\sigma_1 = \sigma_2\,; \; F_1 = F_2 \quad . \quad . \quad . \quad . \quad (6)$$

these being the values of σ and F for the two respective phases. This equality is indeed self-evident in cases where the adsorbed film is completely mobile, as with films on liquids (Rideal); supposing the phases 1 and 2 to be respectively the surface liquid and surface vapour forms of the adsorbed substance, the common F is then simply the "surface vapour pressure" of the former. That equation (6) is also satisfied in other cases may readily be verified. If we suppose on infinitesimal increase $d\omega$ in the area of phase 1 and an equal decrease in that of phase 2, the temperature and total quantity of gas in each adsorbed phase remaining constant, the condition of equilibrium that the Helmholtz free energy ϕ should be a minimum gives us at once[8]

$$d\phi = \sigma_1 d\omega - \sigma_2 d\omega = 0$$

$$\sigma_1 = \sigma_2\,; \; F_1 = F_2 \quad . \quad . \quad . \quad . \quad (6)$$

Variation of *F* with Temperature.

A simplifying assumption made in most theories of adsorption is that the differential heat of adsorption is independent of the degree of covering. It will now be shown that so long as the isotherm is continuous, this assumption necessarily carries the implication that the surface energy lowering F should be directly proportional to the absolute temperature, whatever the nature of the forces acting on the adsorbed molecules.

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[6] *Surface Chemistry* (Cambridge, 1930), 51.

[7] *Proc. Camb. Phil. Soc.*, 1936, **32**, 144; *cf.* also Frenkel, *Z. Physik*, 1924, **26**, 117; Semenoff, *Z. physik. Chem.*, *B*, 1930, **7**, 471.

[8] The Helmholtz free energy of a surface phase of area ω and containing only one adsorbed substance is $\omega(\sigma + \mu\Gamma)$; *cf.* Guggenheim, *Modern Thermodynamics*, 1933, 165, 166, who formulates the various thermodynamic functions relating to surface phases. During the infinitesimal displacement of the boundary here considered $\omega\Gamma$ remains constant, so also μ.

If we write H for the heat content of a system which comprises unit area of a surface phase defined by T and μ and a quantity of free gas in equilibrium with it, we readily obtain for the differential heat of adsorption $-(\partial H/\partial\Gamma)_T$ the relation

$$-(\partial H/\partial\Gamma)_T = -\mu + T(\partial\mu/\partial T)_\Gamma \quad . \quad . \quad . \quad (7)$$

If the gas or vapour be perfect, this reduces to the familiar form

$$-(\partial H/\partial\Gamma)_T = T^2\partial/\partial T(\mu/T) = RT^2(\partial \log p/\partial T)_\Gamma \quad . \quad (8)$$

Differentiating (7) and noting that the condition for a constant differential heat of adsorption is that $\partial^2H/\partial\Gamma^2 = 0$, we have

$$(\partial\mu/\partial\Gamma)_T - T\partial/\partial\Gamma(\partial\mu/\partial T)_\Gamma = (\partial^2H/\partial\Gamma^2)_T = 0 \quad . \quad . \quad (9)$$

$$\therefore (\partial\mu/\partial\Gamma)_T = T\partial/\partial\Gamma(\partial\mu/\partial T)_\Gamma = T\partial/\partial T(\partial\mu/\partial\Gamma)_T.$$

Since $(\partial\mu/\partial\Gamma)_T$ is equal to T times its own temperature coefficient, it must be directly proportional to T

$$(\partial\mu/\partial\Gamma)_T \propto T \quad . \quad . \quad . \quad . \quad . \quad (10)$$

But $(\partial\mu/\partial\Gamma)_T = (\partial\mu/\partial F)_T(\partial F/\partial\Gamma)_T$, and so long as Γ varies continuously with μ we may substitute $1/\Gamma$ for $(\partial\mu/\partial F)_T$, in accordance with the Gibbs equation (1), getting

$$\frac{1}{\Gamma}\left(\frac{\partial F}{\partial\Gamma}\right)_T \propto T.$$

This relation holds for all values of Γ, and we may therefore write

$$F = RT\psi(\Gamma). \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where ψ is independent of T.

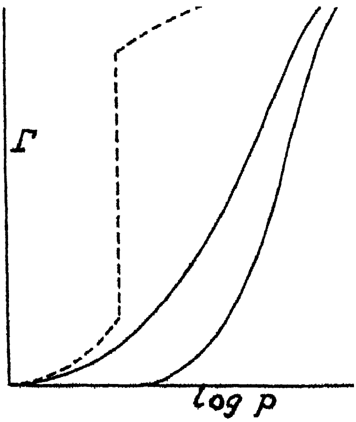

FIG. 1.

In systems where the adsorption energy varies, the following generalisations will necessarily apply so long as only one adsorbed phase is present at a uniform surface:

1. If the differential heat of adsorption increases with the covering ($\partial^2H/\partial\Gamma^2 < 0$), F will increase more rapidly than T; *i.e.*

   $$T(\partial F/\partial T)_\Gamma > F.$$

2. If this heat diminishes with the covering ($\partial^2H/\partial\Gamma^2 > 0$), F will increase less rapidly than T; *i.e.* $T(\partial F/\partial T)_\Gamma < F$.

These relations, which follow when the appropriate signs of inequality are introduced into equations (9) *et seq.*, are readily verified graphically. Let the full lines in the figure represent the semi-logarithmic isotherms at a pair of temperatures. If the differential heat of adsorption is positive and decreases with the covering, then according to (8) the curve for the lower temperature will be uppermost, and the horizontal intercept between the curves will decrease as Γ increases. For any given value of Γ, that of F for each temperature is given, according to (4), by RT times the area between the corresponding curve and the abscissa axis. Since this area is clearly greater in the case of the upper curve (that for the lower temperature), it follows at once that F increases less rapidly than T.

Langmuir's Chemisorption Postulates.

The relations developed in the foregoing section are quite general so long as only one surface phase is present at a uniform surface, but F can be identified as a tangential pressure only if the film is completely mobile. In this section we shall examine the consequences of the specific assumptions from which Langmuir's chemisorption isotherm is derived,[9] namely, that the energy of adsorption should be independent of the covering, and that each adsorbed molecule should fill one and only one "elementary space" on the surface. Fowler[10] has shown that, given these postulates, the isotherm, which for present purposes we may write

$$\frac{\Gamma}{\Gamma_\infty - \Gamma} = \frac{bp}{\Gamma_\infty} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

follows as a necessary thermodynamic consequence. Of the two constants, Γ_∞ is the limiting value of Γ as $p \rightarrow \infty$, and, since it represents the number of "elementary spaces" per unit surface, should be very nearly independent of T; b is the "Henry's law" constant, that is, the limiting value of Γ/p as $p \rightarrow 0$, the form of which is given by Fowler. Using (4) to obtain F, we get

$$F = RT\int_0^p \Gamma d \log p = RT\int_0^\Gamma \Gamma d \log \frac{\Gamma}{\Gamma_\infty - \Gamma} = -RT\Gamma_\infty \log (1 - \Gamma/\Gamma_\infty) \quad (13)$$

This equation, which bears a certain formal similarity to that which gives the osmotic pressure of an ideal solution, is somewhat interesting. Whilst the fraction of the surface covered will, of course, depend on the energy of adsorption as well as on the environmental factors T and μ, it is to be noticed that for a given value of this fraction Γ/Γ_∞, F is actually independent of the chemical nature of the gas. The specific properties of the solid enter only in so far as they determine Γ_∞.

As compared with the very large surface energies which characterise most solids, the lowerings produced by small coverings of chemisorbed molecules are strikingly small. For example, if we take the linear dimensions of the elementary cell to be 3 A. (as a representative figure for atomic lattices) we get at 0° C. for a half-covered surface $F = 29$ dynes, and for one three-quarters covered $F = 58$ dynes per cm.

For small values of Γ/Γ_∞, that is, in the region of obedience to Henry's law, (13) reduces to

$$F = \Gamma RT \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

an equation hitherto considered characteristic of "perfect gas" films in which F is identifiable as a surface pressure.

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[9] *J. Amer. Chem. Soc.*, 1918, **140**, 1361.

[10] *Proc. Camb. Phil. Soc.*, 1935, **31**, 260; the author is grateful to Professor R. H. Fowler for pointing out that the relationship now to be developed follows as a corollary from the analysis given by him.

Physical Adsorption.

In numerous instances where the Langmuir isotherm gives apparent agreement with experiment, the limiting adsorption value or adsorption maximum is characterised by a large negative temperature coefficient.[11] Since the Langmuir form of isotherm (but with Γ_∞ now a function of T) approximately expresses the relation between Γ and p which is to be expected if the film behaves as an imperfect two-dimensional gas,[12] the inference to be drawn here is that the adsorption is essentially physical, the molecules having no definite points of attachment. Where the adsorption is of this type, the surface energy lowering and the surface tension lowering would become equal, and identifiable as a surface pressure. If the differential heat of adsorption is constant, implying the absence of intermolecular forces other than the short-range repulsive ones operative at the moment of collision, the direct proportionality of F to T becomes immediately explicable on kinetic grounds.

The foregoing discussion of *chemi*sorption makes it clear that however great may be the accompanying total energy change, the surface energy cannot be greatly influenced unless the film is nearly complete, or unless strong repulsive forces are acting between the adsorbed molecules. Still less can we look for an effect on the work of stretching which would markedly alter the mechanical properties of the interface. A film of freely mobile molecules, on the other hand, may exert a considerable tangential force. Supposing the film, for example, to contain freely-moving molecules of effective cross-sectional area B = 9A., the surface pressure calculated from the equation of state

$$F(A - B) = RT$$

(which neglects long range intermolecular forces) is 42 dynes at 0° C. when the surface is half-covered, and 84 dynes when it is three-quarters covered.

Long-range repulsive forces, arising from the mutual repulsion of similarly oriented induced dipoles,[13] would affect both the work of forming and the work of stretching the interface. In systems where these forces are important, the heat of adsorption necessarily diminishes markedly as the covering increases.[14] This marked diminution is, however, by no means generally found in systems where adsorbed films play an important part in determining the mechanical properties of solids with large internal surfaces; the effects of water films on such substances as cellulose and wool may be quoted as examples.

In the adsorption of vapours by charcoal, also, long-range repulsive forces do not appear to be of primary importance, for the heat of adsorption often varies but little with the degree of covering.[15] Here the expansion effect discovered by Meehan [16] has been shown experimentally to be directly proportional to the surface *energy* lowering, a relationship hardly to be expected if there is chemisorption. The expansion per mole adsorbed was found to be finite even for the smallest coverings, and to increase at a rate markedly dependent on molecular size.[17] In harmony with the requirements of equation (11), the heat of adsorption of methyl alcohol on the charcoal used in these extensometric experiments has been found independent of the covering over that range of concentrations where the expansion, for a given adsorption, is directly proportional to the absolute temperature.[18] Of interest here also is the evidence of phase transitions, arising from the interplay of adsorptive and intermolecular forces, and of the apparent breakdown of the Gibbs adsorption equation when more than one surface phase is present;[19] unfortunately, the physical imperfections of charcoal obscure these transitions to a marked degree.

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[11] Polanyi, *Z. physik. Chem.*, 1928, **138**, 459; Wilkins and Ward, *ibid.*, 1929, **144**, 259.

[12] Reichenstein, *ibid.*, 1923, **107**, 119; Volmer, *ibid.*, 1925, **115**, 253; Bradley, *Phil. Mag.*, 1931, **11**, 690; *Chem. Rev.*, 1931, **9**, 47.

[13] Langmuir, *J. Amer. Chem. Soc.*, 1932, **54**, 2798; *cf.* Magnus, *Trans. Faraday Soc.*, 1932, **28**, 386.

[14] Langmuir, *loc. cit.*; J. K. Roberts, *Proc. Roy. Soc.*, *A*, 1935, **152**, 445 has shown that the heat of adsorption of hydrogen at a clean uniform surface of tungsten decreases markedly as the surface becomes covered, an effect which he ascribes to the mutual repulsion of induced dipoles.

[15] See, for example, Lamb and Coolidge, *J. Amer. Chem. Soc.*, 1920, **42**, 1146; Cameron, *Trans. Faraday Soc.*, 1930, **26**, 247.

[16] *Proc. Roy. Soc.*, *A*, 1927, **115**, 199.

Summary.

The adsorption of gases has been studied from the point of view of the surface energy and surface tension lowering at the interface. It is shown that where the differential heat of adsorption at a uniform surface is constant, the surface energy lowering for a given molecular adsorption is directly proportional to the absolute temperature, so long as only one surface phase is present; according to the postulates from which Langmuir's chemisorption isotherm is derived it is also independent of the total energy of adsorption, and of the nature of the adsorbed gas. The surface tension, on the other hand, which measures the work of stretching the interface, is affected only if the adsorbed molecules exert a tangential force at the boundary. The surface energy lowering and the surface energy lowering are equal only when the molecules have no fixed points of attachment. It is shown that this physical type of adsorption may play an important part where the mechanical properties of a solid agglomerate depend on the presence of adsorbed films.

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Cairo.

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[17] Bangham, Fakhoury and Mohamed, *Proc. Roy. Soc., A*, 1934, **147**, 152.

[18] Bangham, Fakhoury and Mohamed, *loc. cit.*; the constancy of the differential heat of adsorption in this region has been confirmed by the calorimetric measurements of R. Razouk.

[19] Bangham, Fakhoury and Mohamed, *loc. cit.*

REVIEWS OF BOOKS.

Einführung in Die Theoretische Physik. By R. Fürth. J. Springer, Wien, 1936. Pp. xiv and 483. Price, R.M. 18 and 19.80.

In the space of rather less than five hundred large octavo pages Professor Fürth has managed to compress—without however giving any sense of hurry or crowding—an astonishing amount of ordered information. The book covers the whole field of classical and atomic physics, including statics and dynamics, in a comprehensive and elementary fashion, if the word "elementary" is interpreted as "suited to the reading of undergraduate students in the honours grade."

The text reads straightforwardly and clearly and the book may be commended to the student who would at once improve his physics and his German.

A. F.

Electrical Engineering in Radiology. By L. G. H. SARSFIELD London: Chapman & Hall. Pp. xiii + 284, 190 illustrations. 25s net.

In some forty years X-rays have passed from being a subject of academic study to become a vast and highly specialised industry. A category of persons has arisen for whom the applications are all-important, but who do not profess more than a rudimentary knowledge of radiological engineering. Such workers, whether in medicine, metallurgy, or industry in general therefore need a clear, detailed book which may well save them from catastrophies, major and minor, when "something has gone wrong," or a decision is imperative on a technical point.

Mr. Sarsfield has written exactly what is wanted and moreover inspires confidence by the impression that everything that he records has come under his personal observation and experience. A beginning is made with transformers, and the reader is taken in detail through the problems of rectification, testing, high-voltage transmission, control gear, and the history of the X-ray tube itself. Towards the end, the questions of safety and precautions for workers are reviewed. High potentials are becoming common in physico-chemical laboratories, and the author's warning should not fall upon deaf ears.

The volume is provided with a wealth of illustrations, and is pleasing to read.

F. I. G. R.

Hand- und Jahrbuch der chemischen Physik. Band 9, Abschnitt III. and IV. Von W. HANLE, G. SCHEIBE und W. FROMEL. (Leipzig: Akademische Verlagsgesellschaft M.B.H., 1936. Pp. xvi + 184. Price 18.0 RM. Paper covers.)

The first section of this book, 140 pages in length, deals with the excitation of spectra by light, by material particles, and by heat, and the author examines in detail the elementary processes involved in the various types of atomic and molecular excitation. The nature of the changes in the energy levels, the polarisation of the emitted radiation, and the disturbances due to molecular collisions are fully discussed, and the experimental methods adopted in the examination of the various types of excitation briefly reviewed. Valuable chapters are included on collisions of the second kind, on the production of continuous spectra, and on chemical spectra analysis. The fundamental processes which are described have many bearings on the work of the physical chemist, especially those interested in photochemistry or the kinetics of chemical reactions.

The second section on molecular spectra in solutions and liquids is of more direct application to physical chemistry in that it deals with the nature of the absorption due to the chromophoric groups in the molecule, and how this is affected by the molecular environment. The relationship between the absorption of radiation and chemical constitution and the shift of adsorption bands under the influence of polar substituents in the molecule and of molecules of the solvent has long been a matter of interest to chemists who have sought to use this method to gain information about molecular structure. Such matters are briefly reviewed by the authors as far as this is possible within some 40 pages of text. The examples chosen for discussion are mainly the CO and ethylene bands, and the question of adsorption by ionic molecules is dismissed in a few lines, so that this section is open to the criticism that it can hardly be regarded as a comprehensive survey of the field. It is nevertheless of considerable value in that it gives a clear account of the various factors which must be taken into account in interpreting the absorption spectra of liquids.

W. E. G.

Les Solutions Concentrées: Théorie et Applications aux Mélanges Binaires de Composés Organiques. By Jean Timmermans. (Paris: Masson et Cie, 1936. 25 16·5 cm. 646 pp.

During the past half century a very large amount of attention has been devoted to the experimental investigation and theoretical discussion of the properties of homogeneous mixtures or solutions. In the case of dilute solutions, there exists an extensive literature available for the student and research worker, but in the case of concentrated solutions, this is not so. Although much attention has been paid by quite an army of workers to the investigation of various properties of binary mixtures over a wide or even complete range of concentrations, the results of these investigations are widely scattered and are often difficult to find. We are glad, therefore, to find that these numerous and widely dispersed data have, for the first time, been collected, systematically arranged and critically discussed in the book under review; and as every worker in this field will gladly recognise no one more competent than the author could have been found to carry out this work.

The author has arranged his subject-matter in three main sections, dealing with mixtures of two similar components, mixtures of two components belonging to different groups, and mixtures containing a hydroxylated component. In each section the mixtures are grouped into a number of different classes. In each section and sub-section, a theoretical discussion of the behaviour of the particular class of mixtures precedes the discussion of the experimental results. In this way a complete exposition is given of the behaviour and properties of the whole array of binary mixtures, and the student and research worker gains a knowledge not only of what has been but also of what still remains to be done. Besides a full bibliography relating to each section and sub-section, the behaviour of typical systems is represented by diagrams all of uniform size, reduced from large graphs drawn to scale. This adds greatly to their value.

The author is to be congratulated on a work the excellence of which one cannot but recognise. The discussions are concise but clear, and the author's name is a sufficient guarantee of accuracy. The volume is well indexed and has a most valuable table of systems arranged according to the formulæ of the components, and also a complete bibliography. All workers in the field of concentrated solutions will be grateful to Dr. Timmermans for this excellent and monumental work.

Alex. Findlay.

Handbuch der Experimentalphysik. VOL. XVI., PART I. MAGNETOOPTIK. By W. SCHÜTZ. Akademische Verlagsgesellschaft, Leipzig. (Pp. x and 378. 30 marks ; bound, 32 marks.)

Over twenty years have now elapsed since the appearance of Voigt's well-known monograph on *Magneto- und Elektro-optik*, and of an article on the same subject contributed by him to Graetz's *Handbuch der Elektricität und des Magnetismus*. During this period, the influence of magnetism on light has become an instrument of considerable value in the investigation of atomic and molecular structure, demanding new theories and new mathematical treatments. This change of outlook has been borne in mind by the author of the volume now under review, and he has succeeded in keeping abreast of the rapid development of the subject. Thus, the Zeeman effect, which provided the bulk of the material for the earlier monographs, now requires a whole volume (No. XXII) to itself, and is consequently omitted here ; but in its place, accounts are given of the paramagnetic Faraday effect (known, of course to Voigt, but at that time hardly studied), of the more recent Cotton-Mouton effect, and of the magneto-optical properties of colloidal particles and of coarse suspensions, all of which have formed the basis of contributions to modern physics or physical chemistry.

The first, and longest, section of the volume is devoted to the Faraday effect, including paramagnetic and ferromagnetic as well as diamagnetic rotation. The important measurements at very low temperatures which have been made at Leiden in recent years are described here. The second section deals with transverse magnetic birefringence, in particular with the Cotton-Mouton effect, the third section deals with the optical properties of colloids in a magnetic field, and the final section describes the phenomena which are associated with the reflection of light at the surface of magnetised bodies.

As may be required of a book on experimental physics, purely theoretical sections are reduced to a minimum consistent with comprehensiveness. Adequate accounts of experimental technique are given, together with summaries of the chief results, their relationship with one another, and their significance from the point of view of molecular or atomic physics ; but a true perspective is not always maintained. For example, considerable space is devoted to an account of Allison's magneto-optical method of chemical analysis, which has been criticised and almost universally rejected, and might well have been passed over here with a reference. Nevertheless, in the short space of 378 pages, Schütz has contrived with considerable success to collect and summarise a remarkable amount of valuable information. I[illegible]book which of necessity contains so many references to original lite[illegible]e, however, it is unfortunate that errors should have been allowed to creep in. Thus, " J.C.S." is in places confused with " J.A.C.S." ; and how will Pherson feel without his Mac ?

C. B. A.

ERRATUM.

In the April Issue, lines 14-17 of page 519 should have been placed immediately before the last three lines on page 518.

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